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(54) POSITIVE ELECTRODE PASTE COMPOSITION FOR LITHIUM SECONDARY BATTERY, POSITIVE ELECTRODE, AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a positive electrode paste composition for lithium secondary battery excellent in the performance as required of lithium secondary battery and also suitable for mass-production, provide a positive electrode using the paste composition, and offer a method for manufacturing such positive electrodes.

SOLUTION: A positive electrode active material consisting of lithium-nickel series compound oxide having a stratified crystalline structure, a conductive substance to give conductivity to this active material, and a binder to couple them together are dispersed in a solvent, and thereto 0.1-3 pts.wt. organic acid of divalent or more is added relative to 100 pts.wt. positive electrode active material. This paste composition is applied to an electricity collector followed by drying so that an intended positive electrode for lithium secondary battery is produced.

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**CLAIMS**

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[Claim(s)]

[Claim 1] The positive-electrode paste constituent for lithium secondary batteries which makes a lithium nickel system multiple oxide with lamellar-crystal structure a positive active material, distributes to a solvent this positive active material, the conductive matter which gives conductivity to this active material, and the binder which combines both matter, and is characterized by carrying out 0.1-3 weight section combination of the organic acid more than divalent to the positive-active-material 100 weight section at this.

[Claim 2] The positive electrode for lithium secondary batteries which carries out application dryness of the paste constituent given in the aforementioned claim 1 at a charge collector, and is characterized by the bird clapper.

[Claim 3] The manufacture method of the positive electrode for lithium secondary batteries which distributes a lithium alloy system positive active material, the conductive matter, and a binder to a solvent, carries out 0.1-3 weight section combination of the organic acid more than divalent to the positive-active-material 100 weight section at this, and is characterized by creating a positive-electrode paste, carrying out application dryness and manufacturing this to a charge collector.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the positive electrode for lithium secondary batteries using a positive-electrode paste constituent and it suitable as a positive-electrode material of the lithium secondary battery using a lithium nickel multiple oxide with the stratified rock salt type crystal structure as a positive active material, and its manufacture method in more detail about a lithium secondary battery.

[0002]

[Description of the Prior Art] Adopting as the power supplies which I hear that the high voltage and high-energy density are obtained, and this kind of lithium secondary battery can attain small and lightweight-ization, and it is already put in practical use in the related field of information communication equipment, such as a personal computer and a cellular phone, and are carried in an electric vehicle or a hybrid electric vehicle from a resources problem or an environmental problem has also been advanced considerably practical.

[0003] In such a situation, examination is added, for example, various positive-electrode paste constituents for lithium secondary batteries are also about the positive active material in the constituent. A lithium cobalt multiple oxide ( $\text{LiCoO}_2$ ) is used at the beginning, the lithium manganese system multiple oxide ( $\text{LiMn}_2\text{O}_4$ ) of the spinel type crystal structure is also adopted from cost or a resources problem, and the lithium nickel system multiple oxide ( $\text{LiNiO}_2$ ) which I hear that is further excellent in the charge-and-discharge cycle property in high temperature, and has the stratified rock salt type crystal structure also attracts attention.

[0004] Generally this positive-electrode paste constituent is a positive active material which was mentioned above, and the conductive matter for giving conductivity to this positive active material (metaphor). an electrode material is distributed in the binder solution which melted the organic binder resin to the solvent in the mixed-powder end of acetylene black etc. — making — a positive electrode — a mixture — a slurry — carrying out — this positive electrode — a mixture — application dryness of the slurry is carried out on the charge collector which consists of a metal-electrode foil (for example, aluminum foil) or a metal network, and the application material is further stuck by pressure on a charge collector with a press, and it is considering as the positive-electrode sheet

[0005] moreover, also about a negative-electrode sheet, a negative-electrode active material is distributed in the binder solution which melted the organic binder resin to the solvent similarly — making — a negative electrode — a mixture — it considers as a slurry and is manufacturing by carrying out application dryness and pressing this on a charge collector And a lithium secondary battery is constituted by being immersed in the organic electrolytic solution of a non-drainage system in the state where the separator sheet of the porosity which is insulation and has ionic migration nature was made to infix between a positive-electrode sheet and a negative-electrode sheet.

[0006] As the binder solution used for a positive-electrode paste constituent in such a technical background For example, as shown in JP,6-93025,A or JP,6-172452,A, that by which various kinds of fluoride vinylidene system polymers (PVDF) dissolved this in polar solvents, such as a N-methyl-2-pyrrolidone (NMP) and a dimethylformamide, paying attention to having excelled in chemical resistance, weatherability, resistance to contamination, etc., and being stable to the electrolytic solution of a non-drainage system is known.

[0007] Moreover, as shown in JP,10-255808,A, in case a fluoride vinylidene system polymer is melted to an organic solvent and a binder solution is manufactured for example, carry out \*\* fluoric acid processing of the fluoride vinylidene system polymer by addition of heating or the alkali matter, fluoric acid is made to contain, and there are some which improved the adhesive property of an electrode paste constituent and a charge collector by adding acids other than fluoric acid (organic acid) further.

[0008]

[Problem(s) to be Solved by the Invention] However, for example, it is becoming indispensable that the electrode sheet used for the lithium secondary battery for electric vehicles has thickness as thin as 100 micrometers of dozens of micrometers to numbers, and the thing of a large area is used for it. in such a case — while conveying a charge collector sheet on a mass-production line as a method of being this thin film and manufacturing the electrode sheet of a large area cheaply industrially — the sheet side — an electrode — a mixture — application dryness of the slurry (thing which made the above-mentioned binder solution distribute a powder electrode material etc.) will be carried out, and the method of making the application material stick to a charge collector sheet side by pressure by the roll press further will be taken [0009] And since the fluoride vinylidene system polymer used for the binder solution of the

above-mentioned positive-electrode paste constituent had binding capacity with a powder electrode material, and comparatively weak adhesive strength with a charge collector when such a manufacture method is adopted, phenomena, such as ablation from the charge collector of the electrode binder layer which contains defluxion of powder electrode materials, such as an active material, and these powder electrode material while in use, were seen. When the stratified lithium nickel multiple oxide which is excellent in the cell performance in high temperature as a positive active material especially is used, since binding capacity with a fluoride vinylidene system polymer is very weak, An active material drops out at the time of the press after coating, and adhere to a roll or it exfoliates from a charge collector for the stress generated with a press. There is a problem whose press of a large area becomes impossible, and a large-sized cell like the cell for automobiles was not able to be manufactured so much in the lithium secondary battery using the stratified lithium nickel multiple oxide as a positive active material.

[0010] In order to solve an above-mentioned problem, it is possible to increase the quantity of the fluoride vinylidene system polymer which is a binder. However, although surely increase in quantity of a fluoride vinylidene system polymer brings about improvement in binding capacity or adhesive strength, it has the trouble that the active material concentration in an electrode binder layer falls, and the electric capacity per unit area falls. Moreover, even if it made the quantity of a binder increase in the case of a stratified lithium nickel multiple oxide, improvement in sufficient binding capacity or adhesive strength was not obtained.

[0011] And as a cause which is inferior to binding capacity or adhesive strength in the positive-electrode paste constituent using the stratified lithium nickel multiple oxide, since the bonding strength during combination between 3 persons of a positive-active-material particle, a binder, and a charge collector, i.e., an active material particle-active material particle, between active material particle-binders, between active material particle-charge collectors, and between binder-charge collectors is weak, it is thought that an active material particle drops out, and it adheres to a roll or exfoliates from a charge collector at the time of a roll press.

[0012] Moreover, since the addition of an organic acid is a minute amount according to the binder solution shown in JP,10-255808,A In order for an active material particle to drop out at the time of a roll press, and not to solve too the problem of adhering to a roll or exfoliating from a charge collector sheet but to manufacture this binder solution further Since the process that addition of heating or the alkali matter performs \*\* fluoric acid processing is needed in a fluoride vinylidene system polymer, there is also a problem that the production cost of an electrode sheet becomes high.

[0013] This invention persons thought that the above-mentioned problem generated at the time of a roll press would be solvable, when strengthening further bonding strength between 3 persons of a stratified lithium nickel multiple-oxide particle, a binder, and a charge collector. And as a result of carrying out efforts examination wholeheartedly, while blending the organic acid more than divalent during positive-electrode paste composition, by adjusting the loadings of the organic acid, it finds out that the bonding strength between 3 persons of a stratified lithium nickel multiple-oxide particle, a binder, and a charge collector becomes strong, and the problem of adhesion on the roll of an active material particle is solved, and comes to hit on an idea of this invention.

[0014] When the lithium nickel multiple oxide which is excellent in a cell performance as a positive active material, and can demonstrate a high charge-and-discharge cycle property especially under the operating environment in the high temperature as a power supply for automobiles etc. is used, the technical problem which is going to solve this invention has the good fixing nature to the bonding strength between active materials, or the charge collector of an active material, and it is to offer the positive-electrode paste constituent suitable for carrying out abundant manufacture of the large-sized cell. Moreover, it is in offering the lithium secondary battery using the paste constituent, and its manufacture method.

[0015]

[Means for Solving the Problem] The positive-electrode paste constituent for lithium secondary batteries applied to this invention in order to solve this technical problem The lithium nickel system multiple oxide according to claim 1 which has lamellar-crystal structure like is made into a positive active material. This positive active material, The conductive matter which gives conductivity to this active material, and the binder which combines both matter are distributed to a solvent, and let it be a summary to be characterized by carrying out 0.1-3 weight section combination of the organic acid more than divalent to the positive-active-material 100 weight section at this.

[0016] In this case, a stratified lithium nickel system multiple oxide makes stratified rock salt structure, and the crystal structure has the same crystal structure as a lithium cobalt system multiple oxide. And the lithium manganese system multiple oxide of the spinel type crystal structure is excelled in the charge-and-discharge cycle property in high temperature. This stratified lithium nickel system multiple oxide carries out the designation of the multiple oxide with the transition metals which make a lithium and nickel a principal component, and is empirical-formula  $\text{LiNi}_{1-x}\text{MXO}_2$  (M consists of one sort, such as Ti, Mn, Co, aluminum, Mg, and Ga, or two sorts or more.). The multiple oxide expressed with  $0 \leq x < 1$  can be used. Even if it is the case where any are used as an active material, it is good to use a particle powder-like thing and it is desirable to use the thing of the range of 1-30 micrometers by the particle diameter.

[0017] If proper quantity mixture is carried out and the conductive matter can give conductivity to a positive-electrode layer at a positive active material, there will be especially no limit. For example, one sort or two sorts or more of things can be mixed and used among carbon matter powdery parts, such as carbon black, acetylene black, and a graphite. Moreover, a stable metal powder can also be used by the electrode potential to be used.

[0018] Generally as for a binder, the binder of an organic system is used. This organic binder plays the role which ties the particle of a positive active material and the conductive matter, and it is required from nonaqueous electrolyte etc. that it should be stable and weatherability, chemical resistance, thermal resistance, fire retardancy, etc. should be good. For example, thermoplastic polymer, such as fluorine-containing polymer, such as a tetrafluoroethylene polymer, a fluoride vinylidene polymer, and a fluororubber, polypropylene, and polyethylene, etc. can be used. Moreover, it is also possible to use synthetic-rubber system latexes, such as a styrene-butadiene-rubber latex and a carboxy denaturation styrene-butadiene-rubber latex.

[0019] A solvent also plays the role which adjusts the viscosity of the positive-electrode paste constituent which mixes these and is obtained while playing the role which distributes uniformly a positive active material, the conductive matter, and an organic binder. If it can dry easily [ can dissolve the above-mentioned organic binder and ], it can choose suitably. Specifically, an n-methyl-2-pyrrolidone, a dimethyl formamide, etc. are mentioned.

[0020] And the organic acid more than divalent [ which is blended with this ] plays the role which strengthens the bonding strength between 3 persons of a positive-active-material particle, a binder, and a charge collector, and if meltable to a solvent, there will be especially no limit. For example, in a molecule, it considers as a dicarboxylic acid with two carboxyl groups, and aromatic dicarboxylic acids, such as aliphatic unsaturation dicarboxylic acids, such as aliphatic saturation dicarboxylic acids, such as oxalic acid, a malonic acid, a succinic acid, and a glutaric acid, and a maleic acid, and a phthalic acid, are mentioned. Moreover, tricarballic acid, a benzene tricarboxylic acid, etc. are mentioned as a tricarboxylic acid which has three carboxyl groups in a molecule. And as for the blending ratio of coal of an organic acid, it is desirable to carry out to more than the 0.1 weight section to the positive-active-material 100 weight section in order to fully raise the binding capacity of a positive-active-material particle. Moreover, if an organic acid exceeds 3 weight sections, while the improvement effect of binding capacity will fall, a problem arises for cell performances, such as causing the fall of cell capacity.

[0021] The effect that the organic acid more than divalent strengthens the bonding strength between a positive-active-material particle, a binder, and a charge collector as a large reason Since the organic acid more than divalent has two or more parts in which other matter and combination are possible in 1 molecule, When proper quantity combination of the organic acid more than divalent is carried out, to a positive-electrode paste constituent one bonding site The stratified lithium nickel multiple-oxide particle which is a positive active material in the constituent, The stratified lithium nickel multiple-oxide particle of others [ bonding site / which combined with the conductive matter particle and the binder and remained ], It combines with a conductive matter particle and a binder, and the binding capacity between positive-electrode material is raised, further, the bonding site which remained when it applied to a charge collector combines with a current collection body surface, and it is thought that the adhesion force between positive-electrode material and a charge collector is raised.

[0022] Moreover, the positive electrode for lithium secondary batteries of this invention makes it a summary to carry out application dryness of the paste constituent according to claim 1 at a charge collector. According to this positive electrode for lithium secondary batteries, when it includes in a cell, a high charge-and-discharge cycle property is acquired under the operating environment of high temperature.

[0023] The manufacture method of the positive electrode for lithium secondary batteries which furthermore starts this invention distributes a lithium alloy system positive active material, the conductive matter, and a binder to a solvent, carries out 0.1-3 weight section combination of the organic acid more than divalent to the positive-active-material 100 weight section at this, creates a positive-electrode paste and makes it a summary to carry out application dryness and to manufacture this to a charge collector. The positive electrode for lithium secondary batteries which was excellent in the cell property by this will be manufactured.

[0024]

[Embodiments of the Invention] The gestalt of suitable operation of this invention is explained in detail below.

<the composition of a positive-electrode paste constituent, and the production method> — the positive-electrode paste constituent of this invention consists of an organic binder which combines the stratified lithium nickel multiple-oxide particle which can occlusion emit a lithium, and which is an active material, the conductive matter which gives conductivity to this positive-active-material particle, and these positive-active-material particles and conductive matter, a solvent which makes these a uniform distributed state, and an organic acid more than divalent [ which is further blended with this solvent ] as mentioned above And face manufacturing this positive-electrode paste constituent, mix a positive active material and the conductive matter with an organic binder, a solvent is made to blend and distribute this, an organic acid is added further, and a paste-like positive-electrode plied timber slurry is produced.

[0025] Under the present circumstances, when the whole positive-electrode paste constituent produced is made into 100%, in order to obtain sufficient cell capacity, as for the blending ratio of coal of a positive active material, it is desirable to carry out to more than 30wt%. Moreover, as for the blending ratio of coal of the conductive matter, it is desirable to carry out to more than 2wt%, in order to acquire sufficient conductivity, and in order to acquire sufficient binding property, it is desirable [ the blending ratio of coal / the blending ratio of coal of an organic binder ] to carry out to more than 2wt%. Moreover, as mentioned above, in order to acquire the effect of the improvement in bending of a positive-active-material particle, as for the blending ratio of coal of an organic acid, it is desirable to carry out to more than 0.5wt% to the

positive-active-material 100 weight section, since it is the need more than the 0.1 weight section.

[0026] However, if the conductive matter exceeds 20wt(s)%, an organic binder exceeds 10wt(s)% or an organic acid exceeds 3 weight sections to the positive-active-material 100 weight section, a problem will arise for a cell performance, such as causing the fall of cell capacity. Moreover, if it is desirable to carry out to more than 30wt% and it exceeds 60wt% in order to make it distribute uniformly or to make it a problem produce the aforementioned constituent neither to the homogeneity in coating, nor surface smooth nature, viscosity will become low and problems, like dripping arises at the time of coating will generate the blending ratio of coal of a solvent.

[0027] in order that a positive-electrode paste constituent may secure a good cell performance — each above-mentioned component matter — enough — and it is necessary to knead and distribute uniformly. Therefore, as for a kneading distribution process, it is desirable to carry out using the agitator which has the rotating wing, a ball mill, a medium agitation mill, etc.

[0028] The positive electrode of the <production method of positive electrode> lithium secondary battery carries out coating of the positive-electrode paste constituent adjusted and produced as mentioned above to the front face of a charge collector sheet, and is performed by making a positive-electrode layer form. Metallic foils, such as aluminum, are used for the charge collector sheet used as the base material by which coating is carried out. It is convenient to use the coater of the coating-machine method which can carry out application dryness of the electrode paste constituent as equipment used for coating succeeding a band-like charge collector sheet.

[0029] Since the constituent applied to the application section of a coater is hyperviscosity comparatively, it is desirable to adopt application methods, such as a comma coat, a squeeze coat, a die coat, and a lip coat. Let application thickness of a positive-electrode paste constituent be arbitrary things among 50-500 micrometers.

[0030] In the case of a coating-machine method, the dryer part of a coater is a continuous furnace, and can adopt various things, such as hot blast and infrared radiation, as dryness. As for drying temperature, it is desirable that it is 80 degrees C or more. In the case of less than 80 degrees C, it is because there is a possibility of drying becoming inadequate, and a solvent remaining in a positive-electrode layer, and reducing a cell performance. However, if drying temperature is raised not much too much, dryness advances, and since it is expected that uniform dryness cannot be performed, only a front face will require cautions. And in order to make thickness of an electrode layer into predetermined thickness, to raise electrode density and to raise surface smooth nature further, it presses after dryness. This is effective for raising the energy density of a cell. After carrying out application dryness of the electrode paste on a band-like charge collector sheet as equipment used for a press, generally the roll press which can be pressed continuously is used.

[0031] <the structure of a lithium secondary battery> — the lithium secondary battery using the electrode produced as mentioned above is explained. Generally a lithium secondary battery consists of separator fastened between a positive electrode, a negative electrode, and a positive electrode and a negative electrode, and nonaqueous electrolyte. Below, the component except the positive electrode mentioned above is explained in order.

[0032] Although a metal lithium, a lithium compound, a lithium alloy, etc. can be used for a negative-electrode active material, since there is a problem of the deposit of the dendrite accompanying the repeat of charge and discharge, it is good to replace with these and to make into a negative-electrode active material the powdered carbon material which can occlusion emit a lithium. When making a carbon material into a negative-electrode active material, mix a binder to this carbon material, add a suitable solvent if needed and consider as a negative-electrode paste constituent, and carry out application dryness of this on the front face of negative-electrode charge collector sheets, such as copper foil, like a positive electrode, a negative-electrode layer is made to form, and it produces.

[0033] The material which heat-treated a natural graphite, an artificial graphite, corks, carbon black, vapor-growth carbon, a carbon fiber, the material that carbonized the organic macromolecule system compound, or these, and was mixed as a carbon material which can be used as a negative-electrode active material can mention. In manufacture of a negative electrode, the same thing as a positive electrode or the same method can be used about kneading distribution of the binder to which a negative-electrode active material is made to bind, a solvent, and a negative-electrode paste constituent, and the application dryness method.

[0034] The separator fastened between a positive electrode and a negative electrode separates a positive electrode and a negative electrode, and has the function to hold the electrolytic solution and to pass a lithium ion. Porosity films, such as polyethylene and polypropylene, a nonwoven fabric, or textile fabrics can be used for this separator. It is desirable that the thickness of separator sets to about 10-200 micrometers.

[0035] If it is the quality of a non-matter of chance which has ionic migration nature in order that it may be stable and a lithium ion may carry out electrochemical reaction to this positive active material and a negative-electrode active material to the above-mentioned positive active material and a negative-electrode active material, all can be used for nonaqueous electrolyte. Usually, it is made to dissolve in an organic solvent and the lithium salt which is an electrolyte is used. Specifically, as for the salt which can be used for an electrolyte,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiI}$ ,  $\text{LiBr}$ ,  $\text{LiCl}$ ,  $\text{LiAlCl}_4$ ,  $\text{LiHF}_2$ ,  $\text{LiSCN}$ , and  $\text{LiSO}_3\text{CF}_2$  grade is mentioned.  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ , and  $\text{LiClO}_4$  are [ especially among these ] suitable.

[0036] Although the solvent which dissolves this electrolyte can be chosen arbitrarily, the organic solvent of comparatively a high dielectric constant is used as a suitable thing. For example, one sort or two sorts or



more of solvents, such as nitril, such as sulfur compounds, such as lactone, such as glymes, such as un-annular carbonate, such as annular carbonate, such as ethylene carbonate and propylene carbonate, dimethyl carbonate, and ethyl methyl carbonate, a tetrahydrofuran, and 2-methyl tetrahydrofuran, and gamma-butyl lactone, and a sulfolane, and an acetonitrile, are mentioned. One sort or two sorts or more of mixed solvents chosen especially among these from un-annular carbonate, such as annular carbonate, such as ethylene carbonate and propylene carbonate, dimethyl carbonate, and ethyl methyl carbonate, are used as a suitable thing.

[0037] Moreover, it can replace with the above-mentioned nonaqueous electrolyte, and the inorganic solid electrolyte of the lithium glass of the organic solid electrolyte into which polymers, such as an isocyanate bridge formation object of a polyethylene oxide, polypropylene oxide, and a polyethylene oxide, a phenylene oxide, and phenylene sulfide system polymer, were infiltrated, Li<sub>3</sub>N, LiBCl<sub>4</sub>, Li<sub>4</sub>SiO<sub>4</sub>, and Li<sub>3</sub>BO<sub>3</sub> grade can also be used for the above-mentioned nonaqueous electrolyte as a solid electrolyte.

[0038] As a configuration of the lithium secondary battery constituted as mentioned above, it can consider as various things, such as cylindrical, a core box, a paper type, and a card type. Even if it is the case where which configuration is taken, it considers as the electrode object which made separator fasten to a positive electrode and a negative electrode, and connects using the lead for current collection to the positive-electrode terminal which leads to a positive-electrode charge collector and the negative-electrode charge collector shell exterior, and a negative-electrode terminal etc., this electrode object is sealed in a cell case with nonaqueous electrolyte, and a lithium secondary battery is completed.

[0039] Based on the above-mentioned operation form, the positive-electrode paste constituent was actually produced as an example. Moreover, apart from this, the positive-electrode paste constituent which was specified by this invention and which exists out of range was produced as an example of comparison. The positive electrode was produced by coating dryness and the roll press to the charge collector sheet side using the positive-electrode paste constituent of this example and the example of comparison. The cylinder cell type lithium secondary battery was further actually produced. And cell capacity (initial service capacity) was further compared with the charge-and-discharge cycle property in high temperature (60 degrees C), and it confirmed being [ of the adhesion state of the positive active material to the roll at the time of a press, and the positive-electrode layer after a press ] the adhesion, and that the positive-electrode paste constituent of this invention was effective.

[0040]

[Example] Below, production of the positive-electrode paste constituent of an example and the example of comparison and a positive electrode, manufacture of a cell, and the comparison result of an experimental data are explained in order. Component comparison of each sample offering positive-electrode paste constituent is shown in Table 1.

[0041] <Example 1> The positive-electrode paste constituent of this example 1 based on the operation form of the above-mentioned this invention used the crystal grain child of a lithium nickel multiple oxide for the positive active material, and acetylene black was used for it as conductive matter. Moreover, while using for the organic binder the oxalic acid which has a divalent valence in an organic acid using the fluoride vinylidene polymer (it abbreviates to PVDF hereafter), the n-methyl-2-pyrrolidone (it abbreviates to "NMP" hereafter) was used as a solvent, respectively. Each blending ratio of coal in a positive-electrode paste constituent was adjusted so that oxalic acid might serve as the 0.1 weight section to the lithium nickel multiple-oxide 100 weight section, and acetylene black made NMP46.0wt% the adjustment ratio of each matter to the whole oxalic acid 0.5wt% PVDF2.7wt% 5.4wt(s)% lithium nickel multiple-oxide 45.9wt%.

[0042] Kneading distribution of a positive-electrode paste constituent used the disperser (Ur Travis Comil : product made from eye MEKKUSU). Capacity is 2.0l., this disperser has five stirring disks, and 1.4l. of zirconia beads with a diameter of 2mm is thrown in. The stirring disk was rotated by rotational-speed 1000rpm, and consecutive processing of the positive-electrode paste constituent was carried out by part for 150ml/, and it scattered a kneaded part and considered as the positive-electrode paste. [0043] <Example 2> Positive-electrode paste constituent of this example 2 based on the operation form of the above-mentioned this invention, Except having made the loadings of oxalic acid into 3 weight sections to the lithium nickel multiple-oxide 100 weight section, each component material and production conditions were the same as the example 1, and, as for the blending ratio of coal of each component, acetylene black could be NMP46.0wt% oxalic acid 1.3wt% PVDF2.6wt% 5.3wt(s)% lithium nickel multiple-oxide 44.8wt%.

[0044] An organic acid (oxalic acid) is not blended with the <example 1 of comparison> positive-electrode paste constituent, it is an example 1 and each component material except it, and production conditions are the same. Acetylene black made NMP46.0wt% the blending ratio of coal of each component PVDF2.7wt% 5.4wt(s)% lithium nickel multiple-oxide 45.9wt%.

[0045] Examples 1 and 2, and each component material and production conditions are the same except having made [ more ] the blending ratio of coal of the organic acid in the <example 2 of comparison> positive-electrode paste constituent than a convention. In this example 2 of comparison, the loadings of oxalic acid are made into 4 weight sections to the lithium nickel multiple-oxide 100 weight section. Acetylene black made NMP46.0wt% the blending ratio of coal of each component material oxalic acid 1.8wt% PVDF2.6wt% 5.2wt(s)% lithium nickel multiple-oxide 44.4wt%.

[0046] \*\* and it which blend an organic acid with the <example 3 of comparison> positive-electrode paste constituent are an acetic acid which has a univalent valence, and made the loadings 3 weight sections to the lithium nickel multiple-oxide 100 weight section as well as the case of an example 2. The acetylene black of the blending ratio of coal of each component is NMP46.0wt% acetic-acid 1.3wt% PVDF2.6wt% 5.3wt(s)%

lithium nickel multiple-oxide 44.8wt%.

[0047]

[Table 1]

		本 発 明 品		比 較 品		
		実施例1	実施例2	比較例1	比較例2	比較例3
正極活物質	層状ニッケル活物質	100重量部 (45.9wt%)	100重量部 (44.8wt%)	100重量部 (45.9wt%)	100重量部 (44.4wt%)	100重量部 (44.8wt%)
	導電性物質	(5.4wt%)	(5.3wt%)	(5.4wt%)	(5.2wt%)	(5.3wt%)
有機バインダー	アセチレンブラック	(2.7wt%)	(2.6wt%)	(2.7wt%)	(2.6wt%)	(2.6wt%)
	ポリフッ化ビニリデン	(46.0wt%)	(46.0wt%)	(46.0wt%)	(46.0wt%)	(46.0wt%)
溶 剤	n-メチル-2-ピロリドン	0.1重量部 (0.5wt%)	3重量部 (1.3wt%)	—	4重量部 (1.8wt%)	—
	有機酸	—	—	—	—	3重量部 (1.3wt%)

[0048] In this way, the comma coating machine was used on aluminum foil (width of face of 200mm, a length of 250m) with a thickness of 20 micrometers, the produced positive-electrode paste was dried for 5 minutes at 80 degrees C after the single spread, application dryness was carried out about the rear face as well as the dryness back, and the positive-electrode sheet with a length of 200m with which the order edge was cut and positive-electrode material was applied to both sides was obtained. Next, after performing the roll press by linear pressure 1000 kgf/cm and setting thickness to 100 micrometers, it cut off in the predetermined configuration and the positive electrode was produced.

[0049] Using a meso carbon micro bead as a negative-electrode active material, this was mixed with the fluoride vinylidene polymer (PVDF) which is an organic binder in the negative-electrode paste constituent, and the thing which the n-methyl-2-pyrrolidone (NMP) which is a solvent was made to distribute was used for it. Each blending ratio of coal in a negative-electrode paste constituent could be NMP50.0wt% PVDF5.0wt% meso carbon micro bead 45.0wt%. And the comma coating machine was used on copper foil with



a thickness of 20 micrometers, the negative-electrode paste which carried out kneading distribution like the positive-electrode paste constituent was dried for 5 minutes at 80 degrees C after the single spread, application dryness was carried out about the rear face as well as the dryness back, and the negative-electrode sheet with which negative-electrode material was applied to both sides was obtained. Next, after performing the roll press by linear pressure 1000 kgf/cm and setting thickness to 100 micrometers, it cut off in the predetermined configuration and the negative electrode was produced.

[0050] Next, the separator made from polyethylene with a thickness of 20 micrometers was fastened between the positive electrodes and negative electrodes which were obtained, and it wound up on the swirl, and considered as the cylinder cell, and the cell can with which it fills up with a nonaqueous electrolyte was equipped. What dissolved LiPF<sub>6</sub> in the amount mixed liquor of isochores of ethylene carbonate and diethyl carbonate by concentration 1 mol/l as a supporting electrolyte was used for the electrolytic solution.

[0051] Comparative evaluation of the adhesion of the positive-electrode material to the roll in the roll press after application dryness was carried out by the tape friction test about the positive-electrode paste constituent of the examples 1 and 2 which are <comparison result> this invention articles, and the examples 1, 2, and 3 of comparison which are comparison articles. The tape friction test stuck the cellophane tape on the positive-electrode front face, removes it quickly, carried out visual observation of the field which exfoliated, and evaluated adhesion.

[0052] Furthermore, comparative evaluation of initial service capacity and the charge-and-discharge cycle property in high temperature (60 degrees C) was carried out about the cylinder cell produced using each positive-electrode paste constituent. Initial service capacity performed constant-current charge and discharge of 500mA of charging currents, and 500mA of discharge currents in the range of voltage 3.0-4.1V. Moreover, the charge-and-discharge cycle property in high temperature (60 degrees C) repeated the charge and discharge in this condition, and evaluated it by the service-capacity maintenance factor after the 100 cycles to initial service capacity. These results are shown in Table 2.

[0053]

[Table 2]

正極材料への 正極材料の付着状態	正極材料の 密着性	初期放電容量 (mAh)	放電容量維持率 (%)
付着物なし	正極層内の凝集破壊	1460	99
付着物なし	正極層内の凝集破壊	1440	98
50mで付着物あり	集電体表面での界面破壊	1400	96
付着物なし	正極層内の凝集破壊	1080	92
80mで付着物あり	集電体表面での界面破壊	1420	97

	実施例1	実施例2	比較例1	比較例2	比較例3
	本発明品		比較品		

[0054] As shown in the above-mentioned table 2, with the positive-electrode paste constituent of the example 1 of comparison, the affix was in the roll in the roll press at the 50m press time, the binding property of positive-electrode material was low, positive-electrode material exfoliated from the current collection body surface, and the adhesion to a current collection body surface was also low. Since the organic acid more than divalent was not blended with the positive-electrode paste constituent of the example 1 of comparison, this is because the binding property of positive-electrode material and the adhesion fall occurred.

[0055] Moreover, the service capacity in early stages of the cell produced in the positive-electrode paste constituent of the example 2 of comparison although a binding property and adhesion were equivalent to examples 1 and 2 was as low as 1080mAh(s). Since [ to which an organic acid exceeds 3 weight sections to the positive-active-material 100 weight section ] 4 weight sections combination was carried out, this is considered that the capacity of a cell itself fell by the positive-electrode paste of the example 2 of comparison.

[0056] Moreover, with the positive-electrode paste constituent of the example 3 of comparison, the affix was in the roll at the 80m press time, the binding property of positive-electrode material was low, positive-electrode material exfoliated from the current collection body surface, and the adhesion to a current collection body surface was also low. Since the univalent acetic acid was blended with the positive-electrode paste of the example 3 of comparison as an organic acid, this is considered that the binding property of positive-electrode material and the adhesion fall occurred.

[0057] On the other hand, in the positive-electrode paste constituent of the examples 1 and 2 based on the operation gestalt of this invention, a binding property and adhesion improve by combination of a divalent organic acid, there is no adhesion of positive-electrode material on a roll at the 200m press time, and positive-electrode material did not exfoliate from a current collection body surface. Moreover, the fall of the initial service capacity of the produced cell was not accepted, either. From this result, it was proved that the positive-electrode paste constituent of this invention was a positive-electrode paste constituent excellent in a binding property or adhesion.

[0058] Moreover, also about the charge-and-discharge cycle property in high temperature (60 degrees C), since the lithium nickel multiple oxide was used for the positive active material in a positive-electrode paste constituent, it was checked that any prototype demonstrates a high service-capacity maintenance factor. And it is considered as follows as a matter reaction mechanism that such a result was obtained. Since the organic acid more than divalent has two or more parts in which other matter and combination are possible in 1 molecule. When proper quantity combination of the organic acid more than divalent is carried out, to a positive-electrode paste constituent one bonding site. The stratified lithium nickel multiple-oxide particle which is a positive active material in the constituent, The stratified lithium nickel multiple-oxide particle of others [ bonding site / which combined with the conductive matter particle and the binder and remained ], It combines with a conductive matter particle and a binder, and the binding capacity between positive-electrode material is raised, further, the bonding site which remained when it applied to a charge collector combines with a current collection body surface, and it is thought that the adhesion force between positive-electrode material and a charge collector was raised.

[0059] Alterations various in the range which is not limited to the above-mentioned example at all, and does not deviate from the meaning of this invention are possible for this invention. For example, although the above-mentioned example showed the example of oxalic acid as a divalent organic acid, it is clear from the use of the organic acid of this invention that various kinds of organic acids more than divalent [ of dicarboxylic acids such as the other maleic acid, a malonic acid, and a succinic acid, or a tricarboxylic acid and others ] are applied. Moreover, the conductive matter, a binder, etc. are not limited to the thing of an example. And, of course, the improvement of attaining stabilization of a cell property by replacing some nickel elements by other metallic elements also about a stratified lithium nickel system multiple oxide is possible.

[0060]

[Effect of the Invention] According to the positive-electrode paste constituent of this invention, the stratified lithium nickel system multiple oxide is used for the positive active material. The adhesive property over the charge collector of the paste at the time of electrode sheet manufacture was raised by carrying out proper quantity combination of the organic acid of the multiple valued more than divalent into the constituent it not only excels in the cell properties (charge-and-discharge cycle property etc.) in the high temperature (60 degrees C or more) as a lithium secondary battery, but, and it became possible to lose adhesion on the roll of the paint film at the time of the press after coating. Therefore, from the first, it is suitable also for mass-production nature that it is effective to apply this positive-electrode paste

constituent to the power supply of the electric vehicle put especially on the operating environment in high temperature etc. in respect of a cell performance, and it contributes also to the stability of a cell performance and cheap-izing of a manufacturing cost by there being little exfoliation from the charge collector of a positive active material. this invention is cultivating possibility of using a stratified nickel acid lithium for the use which needs to produce a lot of electrode layers like the rechargeable battery for electric vehicles for a short time.

[0061] Moreover, since the positive electrode for lithium secondary batteries of this invention carries out application dryness of the above-mentioned paste constituent at a charge collector, when this positive electrode is included in a lithium secondary battery, it can demonstrate the cell property excellent in the charge-and-discharge cycle property in high temperature etc.

[0062] According to the manufacture method of the positive electrode for lithium secondary batteries which furthermore starts this invention, the positive electrode of the lithium secondary battery which has an outstanding cell property which was mentioned above is obtained.

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[Translation done.]

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**TECHNICAL FIELD**

[The technical field to which invention belongs] this invention relates to the positive electrode for lithium secondary batteries using a positive-electrode paste constituent and it suitable as a positive-electrode material of the lithium secondary battery using a lithium nickel multiple oxide with the stratified rock salt type crystal structure as a positive active material, and its manufacture method in more detail about a lithium secondary battery.

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PRIOR ART

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[Description of the Prior Art] Adopting as the power supplies which I hear that the high voltage and high-energy density are obtained, and this kind of lithium secondary battery can attain small and lightweight-ization, and it is already put in practical use in the related field of information communication equipment, such as a personal computer and a cellular phone, and are carried in an electric vehicle or a hybrid electric vehicle from a resources problem or an environmental problem has also been advanced considerably practical.

[0003] In such a situation, examination is added, for example, various positive-electrode paste constituents for lithium secondary batteries are also about the positive active material in the constituent. A lithium cobalt multiple oxide ( $\text{LiCoO}_2$ ) is used at the beginning, the lithium manganese system multiple oxide ( $\text{LiMn}_2\text{O}_4$ ) of the spinel type crystal structure is also adopted from cost or a resources problem, and the lithium nickel system multiple oxide ( $\text{LiNiO}_2$ ) which I hear that is further excellent in the charge-and-discharge cycle property in high temperature, and has the stratified rock salt type crystal structure also attracts attention.

[0004] Generally this positive-electrode paste constituent is a positive active material which was mentioned above, and the conductive matter for giving conductivity to this positive active material (metaphor), an electrode material is distributed in the binder solution which melted the organic binder resin to the solvent in the mixed-powder end of acetylene black etc. — making — a positive electrode — a mixture — a slurry — carrying out — this positive electrode — a mixture — application dryness of the slurry is carried out on the charge collector which consists of a metal-electrode foil (for example, aluminum foil) or a metal network, and the application material is further stuck by pressure on a charge collector with a press, and it is considering as the positive-electrode sheet

[0005] moreover, also about a negative-electrode sheet, a negative-electrode active material is distributed in the binder solution which melted the organic binder resin to the solvent similarly — making — a negative electrode — a mixture — it considers as a slurry and is manufacturing by carrying out application dryness and pressing this on a charge collector And a lithium secondary battery is constituted by being immersed in the organic electrolytic solution of a non-drainage system in the state where the separator sheet of the porosity which is insulation and has ionic migration nature was made to infix between a positive-electrode sheet and a negative-electrode sheet.

[0006] As the binder solution used for a positive-electrode paste constituent in such a technical background For example, as shown in JP,6-93025,A or JP,6-172452,A, that by which various kinds of fluoride vinylidene system polymers (PVDF) dissolved this in polar solvents, such as a N-methyl-2-pyrrolidone (NMP) and a dimethylformamide, paying attention to having excelled in chemical resistance, weatherability, resistance to contamination, etc., and being stable to the electrolytic solution of a non-drainage system is known.

[0007] Moreover, as shown in JP,10-255808,A, in case a fluoride vinylidene system polymer is melted to an organic solvent and a binder solution is manufactured for example, carry out \*\* fluoric acid processing of the fluoride vinylidene system polymer by addition of heating or the alkali matter, fluoric acid is made to contain, and there are some which improved the adhesive property of an electrode paste constituent and a charge collector by adding acids other than fluoric acid (organic acid) further.

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EFFECT OF THE INVENTION

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[Effect of the Invention] According to the positive-electrode paste constituent of this invention, the stratified lithium nickel system multiple oxide is used for the positive active material. The adhesive property over the charge collector of the paste at the time of electrode sheet manufacture was raised by carrying out proper quantity combination of the organic acid of the multiple valued more than divalent into the constituent it not only excels in the cell properties (charge-and-discharge cycle property etc.) in the high temperature (60 degrees C or more) as a lithium secondary battery, but, and it became possible to lose adhesion on the roll of the paint film at the time of the press after coating. Therefore, from the first, it is suitable also for mass-production nature that it is effective to apply this positive-electrode paste constituent to the power supply of the electric vehicle put especially on the operating environment in high temperature etc. in respect of a cell performance, and it contributes also to the stability of a cell performance and cheap-izing of a manufacturing cost by there being little exfoliation from the charge collector of a positive active material. this invention is cultivating possibility of using a stratified nickel acid lithium for the use which needs to produce a lot of electrode layers like the rechargeable battery for electric vehicles for a short time.

[0061] Moreover, since the positive electrode for lithium secondary batteries of this invention carries out application dryness of the above-mentioned paste constituent at a charge collector, when this positive electrode is included in a lithium secondary battery, it can demonstrate the cell property excellent in the charge-and-discharge cycle property in high temperature etc.

[0062] According to the manufacture method of the positive electrode for lithium secondary batteries which furthermore starts this invention, the positive electrode of the lithium secondary battery which has an outstanding cell property which was mentioned above is obtained.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, for example, it is becoming indispensable that the electrode sheet used for the lithium secondary battery for electric vehicles has thickness as thin as 100 micrometers of dozens of micrometers to numbers, and the thing of a large area is used for it. in such a case — while conveying a charge collector sheet on a mass-production line as a method of being this thin film and manufacturing the electrode sheet of a large area cheaply industrially — the sheet side — an electrode — a mixture — application dryness of the slurry (thing which made the above-mentioned binder solution distribute a powder electrode material etc.) will be carried out, and the method of making the application material stick to a charge collector sheet side by pressure by the roll press further will be taken [0009] And since the fluoride vinylidene system polymer used for the binder solution of the above-mentioned positive-electrode paste constituent had binding capacity with a powder electrode material, and comparatively weak adhesive strength with a charge collector when such a manufacture method is adopted, phenomena, such as ablation from the charge collector of the electrode binder layer which contains defluxion of powder electrode materials, such as an active material, and these powder electrode material while in use, were seen. When the stratified lithium nickel multiple oxide which is excellent in the cell performance in high temperature as a positive active material especially is used, since binding capacity with a fluoride vinylidene system polymer is very weak, An active material drops out at the time of the press after coating, and adhere to a roll or it exfoliates from a charge collector for the stress generated with a press. There is a problem whose press of a large area becomes impossible, and a large-sized cell like the cell for automobiles was not able to be manufactured so much in the lithium secondary battery using the stratified lithium nickel multiple oxide as a positive active material.

[0010] In order to solve an above-mentioned problem, it is possible to increase the quantity of the fluoride vinylidene system polymer which is a binder. However, although surely increase in quantity of a fluoride vinylidene system polymer brings about improvement in binding capacity or adhesive strength, it has the trouble that the active material concentration in an electrode binder layer falls, and the electric capacity per unit area falls. Moreover, even if it made the quantity of a binder increase in the case of a stratified lithium nickel multiple oxide, improvement in sufficient binding capacity or adhesive strength was not obtained.

[0011] And as a cause which is inferior to binding capacity or adhesive strength in the positive-electrode paste constituent using the stratified lithium nickel multiple oxide, since the bonding strength during combination between 3 persons of a positive-active-material particle, a binder, and a charge collector, i.e., an active material particle-active material particle, between active material particle-binders, between active material particle-charge collectors, and between binder-charge collectors is weak, it is thought that an active material particle drops out, and it adheres to a roll or exfoliates from a charge collector at the time of a roll press.

[0012] Moreover, since the addition of an organic acid is a minute amount according to the binder solution shown in JP,10-255808,A In order for an active material particle to drop out at the time of a roll press, and not to solve too the problem of adhering to a roll or exfoliating from a charge collector sheet but to manufacture this binder solution further Since the process that addition of heating or the alkali matter performs \*\* fluoric acid processing is needed in a fluoride vinylidene system polymer, there is also a problem that the production cost of an electrode sheet becomes high.

[0013] This invention persons thought that the above-mentioned problem generated at the time of a roll press would be solvable, when strengthening further bonding strength between 3 persons of a stratified lithium nickel multiple-oxide particle, a binder, and a charge collector. And as a result of carrying out efforts examination wholeheartedly, while blending the organic acid more than divalent during positive-electrode paste composition, by adjusting the loadings of the organic acid, it finds out that the bonding strength between 3 persons of a stratified lithium nickel multiple-oxide particle, a binder, and a charge collector becomes strong, and the problem of adhesion on the roll of an active material particle is solved, and comes to hit on an idea of this invention.

[0014] When the lithium nickel multiple oxide which is excellent in a cell performance as a positive active material, and can demonstrate a high charge-and-discharge cycle property especially under the operating environment in the high temperature as a power supply for automobiles etc. is used, the technical problem which is going to solve this invention has the good fixing nature to the bonding strength between active materials, or the charge collector of an active material, and it is to offer the positive-electrode paste constituent suitable for carrying out abundant manufacture of the large-sized cell. Moreover, it is in offering the lithium secondary battery using the paste constituent, and its manufacture method.

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MEANS

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[Means for Solving the Problem] The positive-electrode paste constituent for lithium secondary batteries applied to this invention in order to solve this technical problem The lithium nickel system multiple oxide according to claim 1 which has lamellar-crystal structure like is made into a positive active material. This positive active material, The conductive matter which gives conductivity to this active material, and the binder which combines both matter are distributed to a solvent, and let it be a summary to be characterized by carrying out 0.1-3 weight section combination of the organic acid more than divalent to the positive-active-material 100 weight section at this.

[0016] In this case, a stratified lithium nickel system multiple oxide makes stratified rock salt structure, and the crystal structure has the same crystal structure as a lithium cobalt system multiple oxide. And the lithium manganese system multiple oxide of the spinel type crystal structure is excelled in the charge-and-discharge cycle property in high temperature. This stratified lithium nickel system multiple oxide carries out the designation of the multiple oxide with the transition metals which make a lithium and nickel a principal component, and is empirical-formula  $\text{LiNi}_1\text{-XMXO}_2$  (M consists of one sort, such as Ti, Mn, Co, aluminum, Mg, and Ga, or two sorts or more.). The multiple oxide expressed with  $0 \leq x < 1$  can be used. Even if it is the case where any are used as an active material, it is good to use a particle powder-like thing and it is desirable to use the thing of the range of 1-30 micrometers by the particle diameter.

[0017] If optimum dose mixture is carried out and the conductive matter can give conductivity to a positive-electrode layer at a positive active material, there will be especially no limit. For example, one sort or two sorts or more of things can be mixed and used among carbon matter powdery parts, such as carbon black, acetylene black, and a graphite. Moreover, a stable metal powder can also be used by the electrode potential to be used.

[0018] Generally as for a binder, the binder of an organic system is used. This organic binder plays the role which ties the particle of a positive active material and the conductive matter, and it is required from nonaqueous electrolyte etc. that it should be stable and weatherability, chemical resistance, thermal resistance, fire retardancy, etc. should be good. For example, thermoplastic polymer, such as fluorine-containing polymer, such as a tetrafluoroethylene polymer, a fluoride vinylidene polymer, and a fluororubber, polypropylene, and polyethylene, etc. can be used. Moreover, it is also possible to use synthetic-rubber system latexes, such as a styrene-butadiene-rubber latex and a carboxy denaturation styrene-butadiene-rubber latex.

[0019] A solvent also plays the role which adjusts the viscosity of the positive-electrode paste constituent which mixes these and is obtained while playing the role which distributes uniformly a positive active material, the conductive matter, and an organic binder. If it can dry easily [ can dissolve the above-mentioned organic binder and ], it can choose suitably. Specifically, an n-methyl-2-pyrrolidone, a dimethyl formamide, etc. are mentioned.

[0020] And the organic acid more than divalent [ which is blended with this ] plays the role which strengthens the bonding strength between 3 persons of a positive-active-material particle, a binder, and a charge collector, and if meltable to a solvent, there will be especially no limit. For example, in a molecule, it considers as a dicarboxylic acid with two carboxyl groups, and aromatic dicarboxylic acids, such as aliphatic unsaturation dicarboxylic acids, such as aliphatic saturation dicarboxylic acids, such as oxalic acid, a malonic acid, a succinic acid, and a glutaric acid, and a maleic acid, and a phthalic acid, are mentioned. Moreover, tricarballic acid, a benzene tricarboxylic acid, etc. are mentioned as a tricarboxylic acid which has three carboxyl groups in a molecule. And as for the blending ratio of coal of an organic acid, it is desirable to carry out to more than the 0.1 weight section to the positive-active-material 100 weight section in order to fully raise the binding capacity of a positive-active-material particle. Moreover, if an organic acid exceeds 3 weight sections, while the improvement effect of binding capacity will fall, a problem arises for cell performances, such as causing the fall of cell capacity.

[0021] The effect that the organic acid more than divalent strengthens the bonding strength between a positive-active-material particle, a binder, and a charge collector as a large reason Since the organic acid more than divalent has two or more parts in which other matter and combination are possible in 1 molecule, When optimum dose combination of the organic acid more than divalent is carried out, to a positive-electrode paste constituent one bonding site The stratified lithium nickel multiple-oxide particle which is a positive active material in the constituent, The stratified lithium nickel multiple-oxide particle of others [ bonding site / which combined with the conductive matter particle and the binder and remained ], It combines with a conductive matter particle and a binder, and the binding capacity between positive-electrode material is raised, further, the bonding site which remained when it applied to a charge

collector combines with a current collection body surface, and it is thought that the adhesion force between positive-electrode material and a charge collector is raised.

[0022] Moreover, the positive electrode for lithium secondary batteries of this invention makes it a summary to carry out application dryness of the paste constituent according to claim 1 at a charge collector. According to this positive electrode for lithium secondary batteries, when it includes in a cell, a high charge-and-discharge cycle property is acquired under the operating environment of high temperature.

[0023] The manufacture method of the positive electrode for lithium secondary batteries which furthermore starts this invention distributes a lithium alloy system positive active material, the conductive matter, and a binder to a solvent, carries out 0.1-3 weight section combination of the organic acid more than divalent to the positive-active-material 100 weight section at this, creates a positive-electrode paste and makes it a summary to carry out application dryness and to manufacture this to a charge collector. The positive electrode for lithium secondary batteries which was excellent in the cell property by this will be manufactured.

[0024]

[Embodiments of the Invention] The gestalt of suitable operation of this invention is explained in detail below.

<the composition of a positive-electrode paste constituent, and the production method> — the positive-electrode paste constituent of this invention consists of an organic binder which combines the stratified lithium nickel multiple-oxide particle which can occlusion emit a lithium, and which is an active material, the conductive matter which gives conductivity to this positive-active-material particle, and these positive-active-material particles and conductive matter, a solvent which makes these a uniform distributed state, and an organic acid more than divalent [ which is further blended with this solvent ] as mentioned above And face manufacturing this positive-electrode paste constituent, mix a positive active material and the conductive matter with an organic binder, a solvent is made to blend and distribute this, an organic acid is added further, and a paste-like positive-electrode plied timber slurry is produced.

[0025] Under the present circumstances, when the whole positive-electrode paste constituent produced is made into 100%, in order to obtain sufficient cell capacity, as for the blending ratio of coal of a positive active material, it is desirable to carry out to more than 30wt%. Moreover, as for the blending ratio of coal of the conductive matter, it is desirable to carry out to more than 2wt%, in order to acquire sufficient conductivity, and in order to acquire sufficient binding property, it is desirable [ the blending ratio of coal / the blending ratio of coal of an organic binder ] to carry out to more than 2wt%. Moreover, as mentioned above, in order to acquire the effect of the improvement in bending of a positive-active-material particle, as for the blending ratio of coal of an organic acid, it is desirable to carry out to more than 0.5wt% to the positive-active-material 100 weight section, since it is the need more than the 0.1 weight section.

[0026] However, if the conductive matter exceeds 20wt(s)%, an organic binder exceeds 10wt(s)% or an organic acid exceeds 3 weight sections to the positive-active-material 100 weight section, a problem will arise for a cell performance, such as causing the fall of cell capacity. Moreover, if it is desirable to carry out to more than 30wt% and it exceeds 60wt% in order to make it distribute uniformly or to make it a problem produce the aforementioned constituent neither to the homogeneity in coating, nor surface smooth nature, viscosity will become low and problems, like dripping arises at the time of coating will generate the blending ratio of coal of a solvent.

[0027] in order that a positive-electrode paste constituent may secure a good cell performance — each above-mentioned component matter — enough — and it is necessary to knead and distribute uniformly Therefore, as for a kneading distribution process, it is desirable to carry out using the agitator which has the rotating wing, a ball mill, a medium agitation mill, etc.

[0028] The positive electrode of the <production method of positive electrode> lithium secondary battery carries out coating of the positive-electrode paste constituent adjusted and produced as mentioned above to the front face of a charge collector sheet, and is performed by making a positive-electrode layer form. Metallic foils, such as aluminum, are used for the charge collector sheet used as the base material by which coating is carried out. It is convenient to use the coater of the coating-machine method which can carry out application dryness of the electrode paste constituent as equipment used for coating succeeding a band-like charge collector sheet.

[0029] Since the constituent applied to the application section of a coater is hyperviscosity comparatively, it is desirable to adopt application methods, such as a comma coat, a squeeze coat, a die coat, and a lip coat. Let application thickness of a positive-electrode paste constituent be arbitrary things among 50-500 micrometers.

[0030] In the case of a coating-machine method, the dryer part of a coater is a continuous furnace, and can adopt various things, such as hot blast and infrared radiation, as dryness. As for drying temperature, it is desirable that it is 80 degrees C or more. In the case of less than 80 degrees C, it is because there is a possibility of drying becoming inadequate, and a solvent remaining in a positive-electrode layer, and reducing a cell performance. However, if drying temperature is raised not much too much, dryness advances, and since it is expected that uniform dryness cannot be performed, only a front face will require cautions. And in order to make thickness of an electrode layer into predetermined thickness, to raise electrode density and to raise surface smooth nature further, it presses after dryness. This is effective for raising the energy density of a cell. After carrying out application dryness of the electrode paste on a band-like charge collector sheet as equipment used for a press, generally the roll press which can be pressed continuously is used.

[0031] <the structure of a lithium secondary battery> -- the lithium secondary battery using the electrode produced as mentioned above is explained. Generally a lithium secondary battery consists of separator fastened between a positive electrode, a negative electrode, and a positive electrode and a negative electrode, and nonaqueous electrolyte. Below, the component except the positive electrode mentioned above is explained in order.

[0032] Although a metal lithium, a lithium compound, a lithium alloy, etc. can be used for a negative-electrode active material, since there is a problem of the deposit of the dendrite accompanying the repeat of charge and discharge, it is good to replace with these and to make into a negative-electrode active material the powdered carbon material which can occlusion emit a lithium. When making a carbon material into a negative-electrode active material, mix a binder to this carbon material, add a suitable solvent if needed and consider as a negative-electrode paste constituent, and carry out application dryness of this on the front face of negative-electrode charge collector sheets, such as copper foil, like a positive electrode, a negative-electrode layer is made to form, and it produces.

[0033] The material which heat-treated a natural graphite, an artificial graphite, corks, carbon black, vapor-growth carbon, a carbon fiber, the material that carbonized the organic macromolecule system compound, or these, and was mixed as a carbon material which can be used as a negative-electrode active material can mention. In manufacture of a negative electrode, the same thing as a positive electrode or the same method can be used about kneading distribution of the binder to which a negative-electrode active material is made to bind, a solvent, and a negative-electrode paste constituent, and the application dryness method.

[0034] The separator fastened between a positive electrode and a negative electrode separates a positive electrode and a negative electrode, and has the function to hold the electrolytic solution and to pass a lithium ion. Porosity films, such as polyethylene and polypropylene, a nonwoven fabric, or textile fabrics can be used for this separator. It is desirable that the thickness of separator sets to about 10-200 micrometers.

[0035] If it is the quality of a non-matter of chance which has ionic migration nature in order that it may be stable and a lithium ion may carry out electrochemical reaction to this positive active material and a negative-electrode active material to the above-mentioned positive active material and a negative-electrode active material, all can be used for nonaqueous electrolyte. Usually, it is made to dissolve in an organic solvent and the lithium salt which is an electrolyte is used. Specifically, as for the salt which can be used for an electrolyte,  $\text{LiPF}_6$ ,  $\text{LiAsF}_6$ ,  $\text{LiSbF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiClO}_4$ ,  $\text{LiI}$ ,  $\text{LiBr}$ ,  $\text{LiCl}$ ,  $\text{LiAlCl}_4$ ,  $\text{LiHF}_2$ ,  $\text{LiSCN}$ , and  $\text{LiSO}_3\text{CF}_2$  grade is mentioned.  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ , and  $\text{LiClO}_4$  are [ especially among these ] suitable.

[0036] Although the solvent which dissolves this electrolyte can be chosen arbitrarily, the organic solvent of comparatively a high dielectric constant is used as a suitable thing. For example, one sort or two sorts or more of solvents, such as nitril, such as sulfur compounds, such as lactone, such as glymes, such as un-annular carbonate, such as annular carbonate, such as ethylene carbonate and propylene carbonate, dimethyl carbonate, and ethyl methyl carbonate, a tetrahydrofuran, and 2-methyl tetrahydrofuran, and gamma-butyl lactone, and a sulfolane, and an acetonitrile, are mentioned. One sort or two sorts or more of mixed solvents chosen especially among these from un-annular carbonate, such as annular carbonate, such as ethylene carbonate and propylene carbonate, dimethyl carbonate, and ethyl methyl carbonate, are used as a suitable thing.

[0037] Moreover, it can replace with the above-mentioned nonaqueous electrolyte, and the inorganic solid electrolyte of the lithium glass of the organic solid electrolyte into which polymers, such as an isocyanate bridge formation object of a polyethylene oxide, polypropylene oxide, and a polyethylene oxide, a phenylene oxide, and phenylene sulfide system polymer, were infiltrated,  $\text{Li}_3\text{N}$ ,  $\text{LiBCl}_4$ ,  $\text{Li}_4\text{SiO}_4$ , and  $\text{Li}_3\text{BO}_3$  grade can also be used for the above-mentioned nonaqueous electrolyte as a solid electrolyte.

[0038] As a configuration of the lithium secondary battery constituted as mentioned above, it can consider as various things, such as cylindrical, a core box, a paper type, and a card type. Even if it is the case where which configuration is taken, it considers as the electrode object which made separator fasten to a positive electrode and a negative electrode, and connects using the lead for current collection to the positive-electrode terminal which leads to a positive-electrode charge collector and the negative-electrode charge collector shell exterior, and a negative-electrode terminal etc., this electrode object is sealed in a cell case with nonaqueous electrolyte, and a lithium secondary battery is completed.

[0039] Based on the above-mentioned operation form, the positive-electrode paste constituent was actually produced as an example. Moreover, apart from this, the positive-electrode paste constituent which was specified by this invention and which exists out of range was produced as an example of comparison. The positive electrode was produced by coating dryness and the roll press to the charge collector sheet side using the positive-electrode paste constituent of this example and the example of comparison. The cylinder cell type lithium secondary battery was further actually produced. And cell capacity (initial service capacity) was further compared with the charge-and-discharge cycle property in high temperature (60 degrees C), and it confirmed being [ of the adhesion state of the positive active material to the roll at the time of a press, and the positive-electrode layer after a press ] the adhesion, and that the positive-electrode paste constituent of this invention was effective.

[Translation done.]

## \* NOTICES \*

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3. In the drawings, any words are not translated.

## EXAMPLE

[Example] Below, production of the positive-electrode paste constituent of an example and the example of comparison and a positive electrode, manufacture of a cell, and the comparison result of an experimental data are explained in order. Component comparison of each sample offering positive-electrode paste constituent is shown in Table 1.

[0041] <Example 1> The positive-electrode paste constituent of this example 1 based on the operation form of the above-mentioned this invention used the crystal grain child of a lithium nickel multiple oxide for the positive active material, and acetylene black was used for it as conductive matter. Moreover, while using for the organic binder the oxalic acid which has a divalent valence in an organic acid using the fluoride vinylidene polymer (it abbreviates to PVDF hereafter), the n-methyl-2-pyrrolidone (it abbreviates to "NMP" hereafter) was used as a solvent, respectively. Each blending ratio of coal in a positive-electrode paste constituent was adjusted so that oxalic acid might serve as the 0.1 weight section to the lithium nickel multiple-oxide 100 weight section, and acetylene black made NMP46.0wt% the adjustment ratio of each matter to the whole oxalic acid 0.5wt% PVDF2.7wt% 5.4wt(s)% lithium nickel multiple-oxide 45.9wt%.

[0042] Kneading distribution of a positive-electrode paste constituent used the disperser (Ur Travis Comil : product made from eye MEKKUSU). Capacity is 2.0l., this disperser has five stirring disks, and 1.4l. of zirconia beads with a diameter of 2mm is thrown in. The stirring disk was rotated by rotational-speed 1000rpm, and consecutive processing of the positive-electrode paste constituent was carried out by part for 150ml/, and it scattered a kneaded part and considered as the positive-electrode paste.

[0043] <Example 2> Positive-electrode paste constituent of this example 2 based on the operation gestalt of the above-mentioned this invention, Except having made the loadings of oxalic acid into 3 weight sections to the lithium nickel multiple-oxide 100 weight section, each component material and production conditions were the same as the example 1, and, as for the blending ratio of coal of each component, acetylene black could be NMP46.0wt% oxalic acid 1.3wt% PVDF2.6wt% 5.3wt(s)% lithium nickel multiple-oxide 44.8wt%.

[0044] An organic acid (oxalic acid) is not blended with the <example 1 of comparison> positive-electrode paste constituent, it is an example 1 and each component material except it, and production conditions are the same. Acetylene black made NMP46.0wt% the blending ratio of coal of each component PVDF2.7wt% 5.4wt(s)% lithium nickel multiple-oxide 45.9wt%.

[0045] Examples 1 and 2, and each component material and production conditions are the same except having made [ more ] the blending ratio of coal of the organic acid in the <example 2 of comparison> positive-electrode paste constituent than a convention. In this example 2 of comparison, the loadings of oxalic acid are made into 4 weight sections to the lithium nickel multiple-oxide 100 weight section. Acetylene black made NMP46.0wt% the blending ratio of coal of each component material oxalic acid 1.8wt% PVDF2.6wt% 5.2wt(s)% lithium nickel multiple-oxide 44.4wt%.

[0046] \*\* and it which blend an organic acid with the <example 3 of comparison> positive-electrode paste constituent are an acetic acid which has a univalent valence, and made the loadings 3 weight sections to the lithium nickel multiple-oxide 100 weight section as well as the case of an example 2. The acetylene black of the blending ratio of coal of each component is NMP46.0wt% acetic-acid 1.3wt% PVDF2.6wt% 5.3wt(s)% lithium nickel multiple-oxide 44.8wt%.

[0047]

[Table 1]

		本 発 明 品		比 較 品		
		実施例1	実施例2	比較例1	比較例2	比較例3
正極活物質	層状ニッケル活物質	100重量部 (45.9wt%)	100重量部 (44.8wt%)	100重量部 (45.9wt%)	100重量部 (44.4wt%)	100重量部 (44.8wt%)
	導電性物質					
	アセチレンブラック	(5.4wt%)	(5.3wt%)	(5.4wt%)	(5.2wt%)	(5.3wt%)
	有機バインダー					
	ポリフッ化ビニリデン	(2.7wt%)	(2.6wt%)	(2.7wt%)	(2.6wt%)	(2.6wt%)
溶 剤	n-メチル-2-ピロリドン	(46.0wt%)	(46.0wt%)	(46.0wt%)	(46.0wt%)	(46.0wt%)
	有機酸	0.1重量部 (0.5wt%)	3重量部 (1.3wt%)	—	4重量部 (1.8wt%)	—
		—	—	—	—	3重量部 (1.3wt%)

[0048] In this way, the comma coating machine was used on aluminum foil (width of face of 200mm, a length of 250m) with a thickness of 20 micrometers, the produced positive-electrode paste was dried for 5 minutes at 80 degrees C after the single spread, application dryness was carried out about the rear face as well as the dryness back, and the positive-electrode sheet with a length of 200m with which the order edge was cut and positive-electrode material was applied to both sides was obtained. Next, after performing the roll press by linear pressure 1000 kgf/cm and setting thickness to 100 micrometers, it cut off in the predetermined configuration and the positive electrode was produced.

[0049] Using a meso carbon micro bead as a negative-electrode active material, this was mixed with the fluoride vinylidene polymer (PVDF) which is an organic binder in the negative-electrode paste constituent, and the thing which the n-methyl-2-pyrrolidone (NMP) which is a solvent was made to distribute was used for it. Each blending ratio of coal in a negative-electrode paste constituent could be NMP50.0wt% PVDF5.0wt% meso carbon micro bead 45.0wt%. And the comma coating machine was used on copper foil with a thickness of 20 micrometers, the negative-electrode paste which carried out kneading distribution like the positive-electrode paste constituent was dried for 5 minutes at 80 degrees C after the single spread, application dryness was carried out about the rear face as well as the dryness back, and the

negative-electrode sheet with which negative-electrode material was applied to both sides was obtained. Next, after performing the roll press by linear pressure 1000 kgf/cm and setting thickness to 100 micrometers, it cut off in the predetermined configuration and the negative electrode was produced.

[0050] Next, the separator made from polyethylene with a thickness of 20 micrometers was fastened between the positive electrodes and negative electrodes which were obtained, and it wound up on the swirl, and considered as the cylinder cell, and the cell can with which it fills up with a nonaqueous electrolyte was equipped. What dissolved LiPF<sub>6</sub> in the amount mixed liquor of isochores of ethylene carbonate and diethyl carbonate by concentration 1 mol/l as a supporting electrolyte was used for the electrolytic solution.

[0051] Comparative evaluation of the adhesion of the positive-electrode material to the roll in the roll press after application dryness was carried out by the tape friction test about the positive-electrode paste constituent of the examples 1 and 2 which are <comparison result> this invention articles; and the examples 1, 2, and 3 of comparison which are comparison articles. The tape friction test stuck the cellophane tape on the positive-electrode front face, removes it quickly, carried out visual observation of the field which exfoliated, and evaluated adhesion.

[0052] Furthermore, comparative evaluation of initial service capacity and the charge-and-discharge cycle property in high temperature (60 degrees C) was carried out about the cylinder cell produced using each positive-electrode paste constituent. Initial service capacity performed constant-current charge and discharge of 500mA of charging currents, and 500mA of discharge currents in the range of voltage 3.0-4.1V. Moreover, the charge-and-discharge cycle property in high temperature (60 degrees C) repeated the charge and discharge in this condition, and evaluated it by the service-capacity maintenance factor after the 100 cycles to initial service capacity. These results are shown in Table 2.

[0053]

[Table 2]

	正極材料への 正極材料の付着状態	正極材料の 密着性	初期放電容量 (mAh)	放電容量維持率 (%)
例1	付着物なし	正極層内の凝集破壊	1460	99
例2	付着物なし	正極層内の凝集破壊	1440	98
例1	50mで付着物あり	集電体表面での界面破壊	1400	96
例2	付着物なし	正極層内の凝集破壊	1080	92
例3	80mで付着物あり	集電体表面での界面破壊	1420	97



	実施例	実施例	比較例	比較例	比較例
	本発明品		比較品		

[0054] As shown in the above-mentioned table 2, with the positive-electrode paste constituent of the example 1 of comparison, the affix was in the roll in the roll press at the 50m press time, the binding property of positive-electrode material was low, positive-electrode material exfoliated from the current collection body surface, and the adhesion to a current collection body surface was also low. Since the organic acid more than divalent was not blended with the positive-electrode paste constituent of the example 1 of comparison, this is because the binding property of positive-electrode material and the adhesion fall occurred.

[0055] Moreover, the service capacity in early stages of the cell produced in the positive-electrode paste constituent of the example 2 of comparison although a binding property and adhesion were equivalent to examples 1 and 2 was as low as 1080mAh(s). Since [ to which an organic acid exceeds 3 weight sections to the positive-active-material 100 weight section ] 4 weight sections combination was carried out, this is considered that the capacity of a cell itself fell by the positive-electrode paste of the example 2 of comparison.

[0056] Moreover, with the positive-electrode paste constituent of the example 3 of comparison, the affix was in the roll at the 80m press time, the binding property of positive-electrode material was low, positive-electrode material exfoliated from the current collection body surface, and the adhesion to a current collection body surface was also low. Since the univalent acetic acid was blended with the positive-electrode paste of the example 3 of comparison as an organic acid, this is considered that the binding property of positive-electrode material and the adhesion fall occurred.

[0057] On the other hand, in the positive-electrode paste constituent of the examples 1 and 2 based on the operation form of this invention, a binding property and adhesion improve by combination of a divalent organic acid, there is no adhesion of positive-electrode material on a roll at the 200m press time, and positive-electrode material did not exfoliate from a current collection body surface. Moreover, the fall of the initial service capacity of the produced cell was not accepted, either. From this result, it was proved that the positive-electrode paste constituent of this invention was a positive-electrode paste constituent excellent in a binding property or adhesion.

[0058] Moreover, also about the charge-and-discharge cycle property in high temperature (60 degrees C), since the lithium nickel multiple oxide was used for the positive active material in a positive-electrode paste constituent, it was checked that any prototype demonstrates a high service-capacity maintenance factor. And it is considered as follows as a matter reaction mechanism that such a result was obtained. Since the organic acid more than divalent has two or more parts in which other matter and combination are possible in 1 molecule When optimum dose combination of the organic acid more than divalent is carried out, to a positive-electrode paste constituent one bonding site The stratified lithium nickel multiple-oxide particle which is a positive active material in the constituent, The stratified lithium nickel multiple-oxide particle of others [ bonding site / which combined with the conductive matter particle and the binder and remained ], It combines with a conductive matter particle and a binder, and the binding capacity between positive-electrode material is raised, further, the bonding site which remained when it applied to a charge collector combines with a current collection body surface, and it is thought that the adhesion force between positive-electrode material and a charge collector was raised.

[0059] Alterations various in the range which is not limited to the above-mentioned example at all, and does not deviate from the meaning of this invention are possible for this invention. For example, although the above-mentioned example showed the example of oxalic acid as a divalent organic acid, it is clear from the use of the organic acid of this invention that various kinds of organic acids more than divalent [ of dicarboxylic acids such as the other maleic acid, a malonic acid, and a succinic acid, or a tricarboxylic acid and others ] are applied. Moreover, the conductive matter, a binder, etc. are not limited to the thing of an example. And, of course, the improvement of attaining stabilization of a cell property by replacing some nickel elements by other metallic elements also about a stratified lithium nickel system multiple oxide is possible.

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(54) 【発明の名称】 リチウム二次電池用正極ペースト組成物、リチウム二次電池用正極、およびその製造方法

(57) 【要約】

【課題】 リチウム二次電池としての電池性能に優れるのみならず、量産性にも適した正極ペースト組成物、およびそのペースト組成物を用いたリチウム二次電池用正極、さらにはその製造方法を提供すること。

【解決手段】 層状結晶構造をもつリチウムニッケル系複合酸化物を正極活物質とし、この正極活物質と活物質に導電性を付与する導電性物質と、両物質を結合するバインダーとを溶剤に分散し、これに2価以上の有機酸を正極活物質100重量部に対して0.1~3重量部配合している。このペースト組成物を集電体に塗布乾燥することによりリチウム二次電池用正極が得られる。

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## 【特許請求の範囲】

【請求項1】 層状結晶構造をもつリチウムニッケル系複合酸化物を正極活物質とし、この正極活物質と、該活物質に導電性を付与する導電性物質と、両物質を結合するバインダとを溶剤に分散し、これに2価以上の有機酸を正極活物質100重量部に対して0.1～3重量部配合していることを特徴とするリチウム二次電池用正極ペースト組成物。

【請求項2】 前記請求項1に記載のペースト組成物を集電体に塗布乾燥してなることを特徴とするリチウム二次電池用正極。

【請求項3】 リチウム合金系正極活物質と導電性物質とバインダとを溶剤に分散し、これに2価以上の有機酸を正極活物質100重量部に対し0.1～3重量部配合して正極ペーストを作成し、これを集電体に塗布乾燥して製造することを特徴とするリチウム二次電池用正極の製造方法。

## 【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、リチウム二次電池に関し、さらに詳しくは、層状岩塩型結晶構造を持つリチウムニッケル複合酸化物を正極活物質として用いるリチウム二次電池の正極材料として好適な正極ペースト組成物およびそれを用いたリチウム二次電池用正極並びにその製造方法に関するものである。

【0002】

【従来の技術】この種のリチウム二次電池は、高電圧・高エネルギー密度が得られ、小型・軽量化が図れるということで、パソコンや携帯電話等の情報通信機器の関連分野では既に実用化され、また資源問題や環境問題から電気自動車やハイブリッド電気自動車に搭載される電源用に採用することも実用的にかなり進められてきた。

【0003】そのような状況の中で、リチウム二次電池用の正極ペースト組成物も種々検討が加えられ、例えば、その組成物中の正極活物質については、当初リチウムコバルト複合酸化物( $\text{LiCoO}_2$ )が用いられ、コストや資源問題からスピネル型結晶構造のリチウムマンガニ系複合酸化物( $\text{LiMn}_2\text{O}_4$ )も採用され、さらに高温での充放電サイクル特性に優れるということで層状岩塩型結晶構造を持つリチウムニッケル系複合酸化物( $\text{LiNiO}_2$ )も注目されている。

【0004】この正極ペースト組成物は、一般には、上述したような正極活物質と、この正極活物質に導電性を付与するための導電性物質(例えば、アセチレンブラックなど)との混合粉末電極材料を、有機バインダー樹脂を溶剤に溶かしたバインダー溶液中に分散させて正極合剤スラリーとしたものであり、この正極合剤スラリーを金属電極箔(例えば、Al箔)または金属網等からなる集電体上に塗布乾燥し、さらにプレスによりその塗布材料を集電体上に圧着して正極シートとしている。

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【0005】また負極シートについても、負極活物質を同じように有機バインダー樹脂を溶剤に溶かしたバインダー溶液中に分散させて負極合剤スラリーとし、これを集電体上に塗布乾燥し、プレスすることにより製作している。そして正極シートと負極シートとの間に絶縁性の、かつイオン移動性を有する多孔質のセパレータシートを介装させた状態で非水系の有機電解液に浸漬することによりリチウム二次電池が構成されるものである。

【0006】このような技術的背景において、正極ペースト組成物に用いられるバインダー溶液としては、例えば、特開平6-93025号公報や特開平6-172452号公報に示されるように、各種のフッ化ビニリデン系重合体(PVDF)が耐薬品性、耐候性、耐汚染性等に優れ、かつ非水系の電解液に対して安定していることに着目し、これをN-メチル-2-ピロリドン(NMP)、ジメチルホルムアミドなどの極性溶媒に溶解したものが知られている。

【0007】また例えば、特開平10-255808号公報に示されるように、フッ化ビニリデン系重合体を有機溶媒に溶かしてバインダー溶液を製造する際に、フッ化ビニリデン系重合体を加熱あるいはアルカリ物質の添加により脱フッ酸処理してフッ酸を含有させ、更にフッ酸以外の酸(有機酸)を添加することにより電極ペースト組成物と集電体との接着性を改善するようにしたものもある。

【0008】

【発明が解決しようとする課題】しかしながら、例えば、電気自動車用のリチウム二次電池に用いられる電極シートは、厚さが数十 $\mu\text{m}$ から数百 $\mu\text{m}$ と薄く、かつ大面積のものをを用いることが必須となってきた。そのような場合にかかる薄膜で、かつ大面積の電極シートを工業的に安価に製造する方法としては、連続生産ライン上で集電体シートを搬送しながらそのシート面に電極合剤スラリー(前述のバインダー溶液に粉末電極材料等を分散させたもの)を塗布乾燥し、さらにロールプレスによりその塗布材料を集電体シート面に圧着させるという方法が採られることになる。

【0009】そしてこのような製造方法を採用した場合、前述の正極ペースト組成物のバインダー溶液に用いられるフッ化ビニリデン系重合体は、粉末電極材料との結着力や集電体との接着力が比較的に弱いため、使用中に活物質等の粉末電極材料の脱落や、これら粉末電極材料を含む電極合剤層の集電体からの剥離などの現象が見られた。特に、正極活物質として高温での電池性能に優れる層状リチウムニッケル複合酸化物を用いた場合、フッ化ビニリデン系重合体との結着力が非常に弱いため、塗工後のプレス時に、活物質が脱落し、ロールに付着したり、プレスにより発生するストレスで集電体から剥離したりして、大面積のプレスが不可能となる問題があり、層状リチウムニッケル複合酸化物を正極活物質とし

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て用いたリチウム二次電池では、自動車用電池のような大型電池を多量に製造することができなかった。

【0010】上述の問題を解決するために、バインダーであるフッ化ビニリデン系重合体を増量することが考えられる。しかし、フッ化ビニリデン系重合体の増量は、確かに結着力や接着力の向上をもたらすが、電極合剤層中の活物質濃度が低下し、単位面積あたりの電気容量が低下するという問題点がある。また、層状リチウムニッケル複合酸化物の場合、バインダーを増量させても、十分な結着力や接着力の向上が得られなかった。

【0011】そして、層状リチウムニッケル複合酸化物を用いた正極ペースト組成物が結着力や接着力に劣る原因としては、正極活物質粒子、バインダーおよび集電体の3者間の結合、すなわち、活物質粒子-活物質粒子間、活物質粒子-バインダー間、活物質粒子-集電体間およびバインダー-集電体間の結合力が弱いために、ロールプレス時に、活物質粒子が脱落してロールに付着したり、集電体から剥離したりするものと考えられる。

【0012】また特開平10-255808号公報に示されるバインダー溶液によれば、有機酸の添加量が微量であるために、やはりロールプレス時に活物質粒子が脱落してロールに付着したり、集電体シートから剥離するという問題は解消されず、さらにこのバインダー溶液を製造するには、フッ化ビニリデン系重合体を加熱あるいはアルカリ物質の添加により脱フッ酸処理を行なうという工程が必要となるため電極シートの生産コストが高くなるという問題もある。

【0013】本発明者らは、層状リチウムニッケル複合酸化物粒子、バインダー、集電体の3者間の結合力をさらに強くすれば、ロールプレス時に発生する上述の問題を解決できるのではないかと考えた。そして鋭意努力検討した結果、正極ペースト組成中に2価以上の有機酸を配合すると共に、その有機酸の配合量を調整することによって、層状リチウムニッケル複合酸化物粒子、バインダー、集電体の3者間の結合力が強くなって活物質粒子のロールへの付着の問題が解消されることを見出し、本発明を想到するに至ったものである。

【0014】本発明の解決しようとする課題は、正極活物質として電池性能に優れ、特に自動車用電源などとしての高温での使用環境下においても高い充放電サイクル特性を発揮し得るリチウムニッケル複合酸化物を用いた時にも、活物質間の結合力や活物質の集電体への定着性が良く、大型電池を多量製造するのに適した正極ペースト組成物を提供することにある。また、そのペースト組成物を用いたリチウム二次電池およびその製造方法を提供することにある。

【0015】

【課題を解決するための手段】この課題を解決するために本発明に係るリチウム二次電池用正極ペースト組成物は、請求項1に記載のように、層状結晶構造をもつリチ

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ウムニッケル系複合酸化物を正極活物質とし、この正極活物質と、該活物質に導電性を付与する導電性物質と、両物質を結合するバインダーとを溶剤に分散し、これに2価以上の有機酸を正極活物質100重量部に対して0.1～3重量部配合していることを特徴とすることを要旨とするものである。

【0016】この場合に層状リチウムニッケル系複合酸化物は、結晶構造が層状岩塩構造をなすものであり、リチウムコバルト系複合酸化物と同じ結晶構造をもつ。そしてスピネル型結晶構造のリチウムマンガン系複合酸化物よりも高温での充放電サイクル特性に優れる。この層状リチウムニッケル系複合酸化物は、リチウムとニッケルを主成分とする遷移金属との複合酸化物を指称し、組成式 $LiNi_{1-x}MxO_2$  (Mは、Ti、Mn、Co、Al、Mg、Gaなどの1種または2種以上からなる。 $0 \leq x < 1$ )で表される複合酸化物を用いることができる。いずれを活物質として使用する場合であっても、微粒子粉末状のものを使用するのがよく、粒子径で1～30 $\mu m$ の範囲のものを使用するのが好ましい。

【0017】導電性物質は、正極活物質に適量混合して正極層に導電性を付与できるものであれば、特に制限はない。例えば、カーボンブラック、アセチレンブラック、黒鉛等の炭素物質粉末のうち1種または2種以上のものを混合して用いることができる。また、使用する電極電位で安定な金属粉末を用いることもできる。

【0018】バインダーは、有機系のバインダーが一般的に用いられる。この有機バインダーは、正極活物質および導電性物質の粒子を繋ぎ止める役割を果たすもので、非水電解液等に対して安定である必要があり、耐候性、耐薬品性、耐熱性、難燃性等が良好なことが要求される。例えば、テトラフルオロエチレン重合体、フッ化ビニリデン重合体、フッ素ゴム等の含フッ素ポリマー、ポリプロピレン、ポリエチレン等の熱可塑性ポリマー等を用いることができる。また、スチレンブタジエンゴムラテックス、カルボキシ変性スチレンブタジエンゴムラテックス等の合成ゴム系ラテックスを用いることも可能である。

【0019】溶剤は、正極活物質、導電性物質、有機バインダーを均一に分散させる役割を果たすとともに、これらを混合して得られる正極ペースト組成物の粘度を調整する役割をも果たす。上記有機バインダーを溶解可能でかつ容易に乾燥できるものであれば、適宜選択することができる。具体的には、n-メチル-2-ピロリドン、ジメチルフォルムアミド等が挙げられる。

【0020】そして、これに配合される2価以上の有機酸は、正極活物質粒子、バインダー、集電体の3者間の結合力を強める役割を果たすもので、溶剤に可溶であれば特に制限はない。例えば、分子内にカルボキシル基を2個もつジカルボン酸として、シュウ酸、マロン酸、コハク酸、グルタル酸等の脂肪族飽和ジカルボン酸、マレ

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イン酸等の脂肪族不飽和ジカルボン酸、フタル酸等の芳香族ジカルボン酸が挙げられる。また、分子内にカルボキシル基を3個もつトリカルボン酸としては、トリカルバリル酸、ベンゼントリカルボン酸等が挙げられる。そして有機酸の配合割合は、正極活物質粒子の結着力を十分に向上させるために、正極活物質100重量部に対して0.1重量部以上とするのが好ましい。また、有機酸が3重量部を越えると、結着力の向上効果が低下するとともに、電池容量の低下を招く等電池性能に問題が生じる。

【0021】2価以上の有機酸が、正極活物質粒子、バインダー、集電体間の結合力を強める効果が大きい理由としては、2価以上の有機酸は1分子中に他の物質と結合可能な部位を2つ以上有しているため、正極ペースト組成物に2価以上の有機酸を適量配合すると、1つの結合部位が、その組成物中の正極活物質である層状リチウムニッケル複合酸化物粒子、導電性物質粒子、バインダーと結合し、残った結合部位が他の層状リチウムニッケル複合酸化物粒子、導電性物質粒子、バインダーと結合し、正極材料間の結着力を向上させ、さらに、集電体に塗布した場合には、残った結合部位が集電体表面と結合し、正極材料と集電体間の密着力を向上させるものと考えられる。

【0022】また本発明のリチウム二次電池用正極は、請求項1に記載のペースト組成物を集電体に塗布乾燥したものであることを要旨とするものである。このリチウム二次電池用正極によれば、電池に組み込んだ時に高温の使用環境下においても高い充放電サイクル特性が得られる。

【0023】さらに本発明に係るリチウム二次電池用正極の製造方法は、リチウム合金系正極活物質と導電性物質とバインダーとを溶剤に分散し、これに2価以上の有機酸を正極活物質100重量部に対し0.1~3重量部配合して正極ペーストを作成し、これを集電体に塗布乾燥して製造することを要旨とするものである。これにより電池特性に優れたリチウム二次電池用正極が製造されることとなる。

【0024】

【発明の実施の形態】以下に本発明の好適な実施の形態を詳細に説明する。

<正極ペースト組成物の構成および作製方法>前述のように本発明の正極ペースト組成物は、リチウムを吸蔵放出可能な活物質である層状リチウムニッケル複合酸化物粒子と、この正極活物質粒子に導電性を付与する導電性物質と、これらの正極活物質粒子と導電性物質とを結合する有機バインダーと、これらを均一な分散状態とする溶剤と、さらにこの溶剤に配合する2価以上の有機酸とから構成される。そして、この正極ペースト組成物を製造するに際しては、正極活物質と導電性物質を有機バインダーと混合し、これを溶剤に配合して分散させ、さら

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に有機酸を加えてペースト状の正極合材スラリーを作製する。

【0025】この際、正極活物質の配合割合は、作製される正極ペースト組成物の全体を100%とした場合、十分な電池容量を得るために、30wt%以上とするのが望ましい。また、導電性物質の配合割合は、十分な導電性を得るために、2wt%以上とするのが望ましく、有機バインダーの配合割合は、十分な結着性を得るために、2wt%以上とするのが望ましい。また、有機酸の配合割合は、前述したように、正極活物質粒子の結着性向上の効果を得るために、正極活物質100重量部に対して0.1重量部以上必要であるので0.5wt%以上とするのが望ましい。

【0026】但し、導電性物質が20wt%を越えたり、有機バインダーが10wt%を越えたり、有機酸が正極活物質100重量部に対して3重量部を越えたりすると、電池容量の低下を招く等、電池性能に問題が生じる。また、溶剤の配合割合は、前記組成物を均一に分散させたり、塗工での均一性や表面平滑性等に問題が生じないようにするために、30wt%以上とすることが望ましく、60wt%を越えると、粘度が低くなり、塗工時にタレが生じる等の問題が発生する。

【0027】正極ペースト組成物は、良好な電池性能を確保するため、上記各成分物質が充分にかつ均一に、混練、分散されている必要がある。したがって、混練分散工程は回転する羽根を有する攪拌機、ボールミル、媒体攪拌ミル等を用いて行うのが望ましい。

【0028】<正極の作製方法>リチウム二次電池の正極は、上記のように調整、作製された正極ペースト組成物を集電体シートの表面に塗工し、正極層を形成させることによって行われる。塗工される基材となる集電体シートには、アルミニウム等の金属箔が用いられる。塗工に用いられる装置としては、帯状の集電体シートに連続して電極ペースト組成物を塗布乾燥できるコーター方式の塗工機を用いるのが便利である。

【0029】塗工機の塗布部には、塗布する組成物が比較的高粘度であることから、コンマコート、スクイズコート、ダイコート、リップコート等の塗布方式を採用するのが好ましい。正極ペースト組成物の塗布厚さは、50~500μmの間で任意のものとすることができ

【0030】塗工機の乾燥部は、コーター方式の場合連続炉であって、乾燥には、熱風、赤外線等種々のものが採用できる。乾燥温度は、80℃以上であることが好ましい。80℃未満の場合は、乾燥が不十分となり、正極層内に溶剤が残留する可能性があり、電池性能を低下させるおそれがあるからである。ただし、あまり乾燥温度を上げすぎると表面のみ乾燥が進行し、均一な乾燥ができないことが予想されるため注意を要する。そして電極層の膜厚を所定の厚さとし、電極密度を高め、さらに表

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面平滑性を高めるため、乾燥後にプレスを行う。これは、電池のエネルギー密度を高めるのに効果的である。プレスに用いられる装置としては、帯状の集電体シート上に電極ペーストを塗布乾燥した後、連続的にプレスできるロールプレスが一般的に用いられる。

【0031】<リチウム二次電池の構造>上記のように作製した電極を用いたリチウム二次電池について説明する。リチウム二次電池は一般に、正極と、負極と、正極と負極との間に挟装されるセパレータと、非水電解液とから構成される。以下に、上述した正極を除いた構成要素について順に説明する。

【0032】負極活物質には、金属リチウム、リチウム化合物、リチウム合金等を使用できるが、充放電の繰り返しに伴うデンドライトの析出という問題があるため、これらに代え、リチウムを吸蔵放出可能な粉末状の炭素材料を負極活物質とするのが良い。炭素材料を負極活物質とする場合、この炭素材料にバインダーを混合し、必要に応じて適当な溶剤を加えて負極ペースト組成物とし、これを正極同様、銅箔等の負極集電体シートの表面に塗布乾燥し、負極層を形成させて作製する。

【0033】負極活物質として用いることのできる炭素材料としては、天然黒鉛、人造黒鉛、コークス、カーボンブラック、気相成長炭素、炭素繊維、有機高分子系化合物を炭素化した材料、またはこれらを熱処理、混合した材料等が挙げることができる。負極の製作にあたっては、負極活物質を結着させるバインダー、溶剤、負極ペースト組成物の混練分散、塗布乾燥方法等については、正極と同様のものを、または同様の方法を用いることができる。

【0034】正極と負極との間に挟装されるセパレータは、正極と負極とを分離し、電解液を保持してリチウムイオンを通過させる機能を有するものである。このセパレータには、ポリエチレン、ポリプロピレン等の多孔質フィルム、不織布または織布等を用いることができる。セパレータの厚さが10～200μm程度とすることが好ましい。

【0035】非水電解液には、上記正極活物質および負極活物質に対して安定であり、かつリチウムイオンがこの正極活物質および負極活物質と電気化学反応するためイオン移動性を有する非水物質であれば、いずれも使用することができる。通常は、電解質であるリチウム塩を有機溶媒に溶解させて用いる。電解質に使用できる塩は、具体的には、 $\text{LiPF}_6$ 、 $\text{LiAsF}_6$ 、 $\text{LiSbF}_6$ 、 $\text{LiBF}_4$ 、 $\text{LiClO}_4$ 、 $\text{LiI}$ 、 $\text{LiBr}$ 、 $\text{LiCl}$ 、 $\text{LiAlCl}_4$ 、 $\text{LiHF}_2$ 、 $\text{LiSCN}$ 、 $\text{LiSO}_3\text{CF}_2$ 等が挙げられる。これらのうちで特に、 $\text{LiPF}_6$ 、 $\text{LiBF}_4$ 、 $\text{LiClO}_4$ が好適である。

【0036】この電解質を溶解する溶媒は任意に選択できるが、比較的高誘電率の有機溶媒が好適なものとして用いられる。例えば、エチレンカーボネート、プロピレ

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ンカーボネート等の環状カーボネート類、ジメチルカーボネート、エチルメチルカーボネート等の非環状カーボネート類、テトラヒドロフラン、2-メチルテトラヒドロフラン等のグライム類、γ-ブチラクトン等のラクトン類、スルフォラン等の硫黄化合物、アセトニトリル等のニトリル類等の1種または2種以上の溶媒が挙げられる。これらのうちで特に、エチレンカーボネート、プロピレンカーボネート等の環状カーボネート類、ジメチルカーボネート、エチルメチルカーボネート等の非環状カーボネート類から選ばれた1種または2種以上の混合溶媒が好適なものとして用いられる。

【0037】また、上記非水電解液に代えて固体電解質として、上記非水電解液を例えばポリエチレンオキサイド、ポリプロピレンオキサイド、ポリエチレンオキサイドのイソシアネート架橋体、フェニレンオキシド、フェニレンスルフィド系ポリマー等の重合体に含浸させた有機固体電解質、 $\text{Li}_3\text{N}$ 、 $\text{LiBCl}_4$ 、 $\text{Li}_4\text{SiO}_4$ 、 $\text{Li}_3\text{BO}_3$ 等のリチウムガラスの無機固体電解質を使用することもできる。

【0038】以上のように構成されるリチウム二次電池の形状としては、円筒型、箱型、ペーパー型、カード型等、種々のものとして行うことができる。いずれの形状を採用する場合であっても、正極および負極にセパレータを挟装させた電極体とし、正極集電体および負極集電体から外部に通ずる正極端子および負極端子までの集電用リード等を用いて接続し、この電極体を非水電解液とともに電池ケースに密閉して、リチウム二次電池を完成させる。

【0039】上記の実施形態に基づいて、実施例として、実際に正極ペースト組成物を作製した。また、これとは別に、本発明で規定した範囲外にある正極ペースト組成物を、比較例として作製した。この実施例および比較例の正極ペースト組成物を用いて集電体シート面に塗工乾燥・ロールプレスにより正極を作製した。さらに実際に円筒セル型のリチウム二次電池を作製した。そして、プレス時のロールへの正極活物質の付着状態、プレス後の正極層の密着性、さらに電池容量（初期放電容量）と高温（60℃）での充放電サイクル特性を比較して、本発明の正極ペースト組成物が有効なものであることを確かめた。

【0040】

【実施例】以下に、実施例および比較例の正極ペースト組成物、正極の作製、電池の製作、及び実験データの比較結果について順に説明する。各供試正極ペースト組成物の成分比較を表1に示す。

【0041】<実施例1>上記した本発明の実施形態に基づくこの実施例1の正極ペースト組成物は、正極活物質にリチウムニッケル複合酸化物の結晶粒子を用い、導電性物質としてアセチレンブラックを用いた。また有機バインダーにはフッ化ビニリデン重合体（以下、PVD Fと略す）を用い、有機酸には2価の原子価を有するシ



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シュウ酸を用いると共に、溶剤としてn-メチル-2-ピロリドン（以下、「NMP」と略す）をそれぞれ用いた。正極ペースト組成物におけるそれぞれの配合割合は、リチウムニッケル複合酸化物100重量部に対してシュウ酸が0.1重量部となるように調整し、全体に対する各物質の調整比率は、リチウムニッケル複合酸化物45.9wt%、アセチレンブラックが5.4wt%、PVDF2.7wt%、シュウ酸0.5wt%、NMP46.0wt%とした。

【0042】正極ペースト組成物の混練分散は、分散機（ウルトラビスコミル；アイメックス製）を用いた。本分散機は、容量が2.0リットルで、攪拌ディスクが5枚あり、直径2mmのジルコニアビーズが1.4リットル投入されている。攪拌ディスクを回転速度1000rpmで回転させ、150ml/分で正極ペースト組成物を連続処理して混練分散し、正極ペーストとした。

【0043】＜実施例2＞上記した本発明の実施形態に基づくこの実施例2の正極ペースト組成物は、シュウ酸の配合量をリチウムニッケル複合酸化物100重量部に対して3重量部とした以外は、実施例1と各成分材料、作製条件は同じであって、各成分の配合割合は、リチウムニッケル複合酸化物44.8wt%、アセチレンブラックが5.3wt%、PVDF2.6wt%、シュウ酸1.3wt%、NMP46.0wt%とした。

【0044】＜比較例1＞正極ペースト組成物に有機酸

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（シュウ酸）を配合しないものであって、それ以外は実施例1と各成分材料、作製条件は同じである。各成分の配合割合は、リチウムニッケル複合酸化物45.9wt%、アセチレンブラックが5.4wt%、PVDF2.7wt%、NMP46.0wt%とした。

【0045】＜比較例2＞正極ペースト組成物における有機酸の配合割合を規定よりも多くした以外は実施例1および2と各成分材料、作製条件が同一である。この比較例2では、シュウ酸の配合量をリチウムニッケル複合酸化物100重量部に対して4重量部としている。各成分材料の配合割合は、リチウムニッケル複合酸化物44.4wt%、アセチレンブラックが5.2wt%、PVDF2.6wt%、シュウ酸1.8wt%、NMP46.0wt%とした。

【0046】＜比較例3＞正極ペースト組成物に有機酸を配合するも、それは1価の原子価を有する酢酸であって、その配合量は実施例2の場合と同じくリチウムニッケル複合酸化物100重量部に対して3重量部とした。各成分の配合割合は、リチウムニッケル複合酸化物44.8wt%、アセチレンブラックが5.3wt%、PVDF2.6wt%、酢酸1.3wt%、NMP46.0wt%である。

【0047】

【表1】



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	本 発 明 品		比 較 品		
	実施例1	実施例2	比較例1	比較例2	比較例3
正極活物質	100重量部 (45.9wt%)	100重量部 (44.8wt%)	100重量部 (45.9wt%)	100重量部 (44.4wt%)	100重量部 (44.8wt%)
腐食性物質					
アセチレンブラック	(5.4wt%)	(5.3wt%)	(5.4wt%)	(5.2wt%)	(5.3wt%)
有機バインダー					
ポリフッ化ビニリデン	(2.7wt%)	(2.6wt%)	(2.7wt%)	(2.6wt%)	(2.6wt%)
溶 剤					
n-メチル-2-ピロリドン	(46.0wt%)	(46.0wt%)	(46.0wt%)	(46.0wt%)	(46.0wt%)
有 機 酸	0.1重量部 (0.5wt%)	3重量部 (1.3wt%)	—	4重量部 (1.8wt%)	—
	—	—	—	—	3重量部 (1.3wt%)

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【0048】こうして作製された正極ペーストを厚さ20 $\mu$ mのアルミ箔(幅200mm、長さ250m)上にコンマコーターを用いて片面塗布後、80℃で5分間乾燥し、乾燥後同様に裏面についても塗布乾燥し、前後端をカットして両面に正極材料が塗布された長さ200mの正極シートを得た。次に、線圧1000kgf/cmでロールプレスを行い、膜厚を100 $\mu$ mとした後、所定の形状に切り取り、正極を作製した。

【0049】負極ペースト組成物には、負極活物質としてメソカーボンマイクロビーズを用い、これを有機バインダーであるフッ化ビニリデン重合体(PVDF)と混

40 合し、溶剤であるn-メチル-2-ピロリドン(NMP)に分散させたものを用いた。負極ペースト組成物におけるそれぞれの配合割合は、メソカーボンマイクロビーズ45.0wt%、PVDF5.0wt%、NMP50.0wt%とした。そして正極ペースト組成物と同様にして混練分散した負極ペーストを厚さ20 $\mu$ mの銅箔上にコンマコーターを用いて片面塗布後、80℃で5分間乾燥し、乾燥後同様に裏面についても塗布乾燥し、両面に負極材料が塗布された負極シートを得た。次に、線圧1000kgf/cmでロールプレスを行い、膜厚を100 $\mu$ mとした後、所定の形状に切り取り、負極を作

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製した。

【0050】次に、得られた正極と負極の間に厚さ20  $\mu\text{m}$ のポリエチレン製セパレーターを挟装して、渦巻上に巻き上げて円筒セルとし、非水系電解液が充填される電池缶に装着した。電解液は、エチレンカーボネートとジエチルカーボネートの等容量混合液に、支持塩として  $\text{LiPF}_6$  を濃度  $1\text{mol/l}$  で溶解したものをを用いた。

【0051】＜比較結果＞本発明品である実施例1および2、比較品である比較例1、2および3の正極ペースト組成物について、塗布乾燥後のロールプレスにおけるロールへの正極材料の密着性をテープ剥離試験で比較評価した。テープ剥離試験は、正極表面にセロハンテープ

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を貼り付け、すばやく剥がすものであり、剥離した面を目視観察して密着性を評価した。

【0052】さらに、それぞれの正極ペースト組成物を用いて作製した円筒セルについて、初期放電容量および高温度(60℃)での充放電サイクル特性を比較評価した。初期放電容量は、充電電流500mA・放電電流50.0mAの定電流充放電を、電圧3.0~4.1Vの範囲で行なった。また高温度(60℃)での充放電サイクル特性は、この条件での充放電を繰り返し、初期放電容量に対する100サイクル後の放電容量維持率で評価した。これらの結果を表2に示す。

【0053】

【表2】

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	プレスロールへの 正極材料の付着状態	正極材料の 密着性	初期放電容量 (mAh)	放電容量維持率 (%)
実施例1	付着物なし	正極層内の凝集破壊	1460	99
実施例2	付着物なし	正極層内の凝集破壊	1440	98
比較例1	50mで付着物あり	集電体表面での界面破壊	1400	96
比較例2	付着物なし	正極層内の凝集破壊	1080	92
比較例3	80mで付着物あり	集電体表面での界面破壊	1420	97
本発明品				
比較品				

【0054】上記表2に示すように、比較例1の正極ペースト組成物では、ロールプレスにおいて50mプレス時点でロールに付着物があって正極材料の結着性が低く、集電体表面から正極材料が剥離して集電体表面に対する密着性も低かった。これは、比較例1の正極ペースト組成物には2価以上の有機酸が配合されていなかったために、正極材料の結着性や密着性低下が発生したことによる。

【0055】また、比較例2の正極ペースト組成物では、結着性や密着性は実施例1および2と同等であったが、作製した電池の初期の放電容量が1080mAhと

低かった。これは、比較例2の正極ペーストには有機酸が、正極活物質100重量部に対して3重量部を越える4重量部配合されていたために、電池の容量自体が低下したものと考えられる。

【0056】また、比較例3の正極ペースト組成物では、80mプレス時点でロールに付着物があり、正極材料の結着性が低く、集電体表面から正極材料が剥離し、集電体表面に対する密着性も低かった。これは、比較例3の正極ペーストには有機酸として1価の酢酸が配合されていたために、正極材料の結着性や密着性低下が発生したものと考えられる。

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【0057】これに対して、本発明の実施形態に基づいた実施例1および2の正極ペースト組成物では、2価の有機酸の配合により結着性や密着性が向上し、200mプレス時点でロールへの正極材料の付着がなく、正極材料が集電体表面から剥離することもなかった。また、作製した電池の初期放電容量の低下も認められなかった。この結果から、本発明の正極ペースト組成物は、結着性や密着性に優れた正極ペースト組成物であることが実証された。

【0058】また高温（60℃）での充放電サイクル特性についても、正極ペースト組成物中の正極活物質にリチウムニッケル複合酸化物を用いているために、いずれの試作品も高い放電容量維持率を発揮することが確認された。そして、このような結果が得られたことは、物質反応メカニズムとして次のように考察される。2価以上の有機酸は、1分子中に他の物質と結合可能な部位を2つ以上有しているため、正極ペースト組成物に2価以上の有機酸を適量配合すると、1つの結合部位が、その組成物中の正極活物質である層状リチウムニッケル複合酸化物粒子、導電性物質粒子、バインダーと結合し、残った結合部位が他の層状リチウムニッケル複合酸化物粒子、導電性物質粒子、バインダーと結合し、正極材料間の結着力を向上させ、さらに、集電体に塗布した場合には、残った結合部位が集電体表面と結合し、正極材料と集電体間の密着力を向上させたものと考えられる。

【0059】本発明は、上記した実施例に何ら限定されるものではなく、本発明の趣旨を逸脱しない範囲で種々の改変が可能である。例えば、上記実施例では、2価の有機酸としてシュウ酸の例を示したが、それ以外のマレイン酸、マロン酸、コハク酸などのジカルボン酸類、あるいはトリカルボン酸その他の2価以上の各種の有機酸が適用されることは、本発明の有機酸の効用から明らか

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なことである。また、導電性物質、バインダー等も実施例のものに限定されるものではない。そして層状リチウムニッケル系複合酸化物についても、ニッケル元素の一部を他の金属元素に置換することにより電池特性の安定化を図る等の改善は勿論可能である。

【0060】

【発明の効果】本発明の正極ペースト組成物によれば、正極活物質に層状リチウムニッケル系複合酸化物を用いていることによりリチウム二次電池としての高温（60℃以上）での電池特性（充放電サイクル特性など）に優れるばかりでなく、その組成物中に2価以上の多価の有機酸を適量配合することで電極シート製造時におけるペーストの集電体に対する接着性を向上させ、塗工後のプレス時の塗膜のロールへの付着をなくすることが可能となった。そのためこの正極ペースト組成物を、特に高温での使用環境に置かれる電気自動車の電源などに適用することは電池性能面で有効であることはもとより、量産性にも適して正極活物質の集電体からの剥脱が少ないことによる電池性能の安定性と製造コストの低廉化にも寄与するものである。本発明は、電気自動車用二次電池のように短時間に多量の電極層を作製する必要がある用途に、層状ニッケル酸リチウムを用いる可能性を拓くものとなっている。

【0061】また本発明のリチウム二次電池用正極は、上記ペースト組成物を集電体に塗布乾燥したものであるから、リチウム二次電池にこの正極を組み込んだ時に高温での充放電サイクル特性などに優れた電池特性を発揮することができる。

【0062】さらに本発明に係るリチウム二次電池用正極の製造方法によれば、上述したような優れた電池特性を有するリチウム二次電池の正極が得られるものである。

フロントページの続き

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